MANUAL OF AGRICULTURAL CHEMISTRY

HERBERT INGLE

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Cornell University

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MANUAL OF
AGRICULTURAL CHEMISTRY.

BY

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WITH 11 ILLUSTRATIONS.

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PREFACE.

THE present volume is based upon lectures delivered annually, for several years past, by the author, to classes of agricultural students, many of whom had already acquired some knowledge of general chemistry. There has always been difficulty in finding a text-book suited to the requirements of such students. An attempt has therefore been made in this work to present to the reader some, at least, of the many problems of agriculture on which chemistry and physics may throw light. In all cases the writer has endeavoured to avoid empiric statements, and to give, as far as possible, an explanation of the facts or phenomena described.

Current literature has been freely consulted, and, whenever possible, reference to the source of the information has been given. In some few instances, perhaps, this may not have been done, for in the preparation of lecture notes it often happens that matter is incorporated without a record of its origin being made. In most cases the original paper is named, and, if foreign, the abstract in the Journal of the Chemical Society or in the Journal of the Society of Chemical Industry has, if possible, also been quoted.

Much originality is not expected in a manual, except, perhaps, in the arrangement and order of the subject matter; but the author ventures to hope that not only is the book novel in scope and style, but that certain views therein expressed are original and may prove of service. Thus, in the introductory chapter, the account of the distribution and relative abundance of the elements contains some ideas not, so far as he is aware, to be found elsewhere. Chapters IV., X., and XIV., too, will be found to contain matter not generally available.

Osmosis and diffusion appear to be commonly regarded by botanists as synonymous terms, and much confusion seems to exist as to the parts which osmotic pressure and diffusion play in the processes of plant life. In the tenth chapter an attempt has been made to explain the essential differences between free diffusion through a porous membrane and the setting up of osmotic pressure when solutions of different concentration are separated by a semi-permeable membrane, and to point out the application of the knowledge of these phenomena to the particular case of a plant's roots.

In the description of Brown and Escombe's valuable researches on the manner in which carbon dioxide is assimilated by plants, through the stomata of the leaves, the author has ventured to explain the results by a method which he devised in 1899, and which is based on the generally accepted kinetic theory of gases.

The book does not profess to be a laboratory manual, but in several instances accounts of various analytical processes, applicable to agricultural products, are given with a view of enabling the reader to understand and appreciate the results of analyses. Most of these processes are such as the author himself uses, and certain little modifications which he has found useful are described.

PREFACE.

The diagrams are of simple character, intended to show as clearly as possible the particular points desired. Those on pages 324 to 327 are from blocks kindly lent by the Highland and Agricultural Society of Scotland, to whom the author desires to express his thanks.

The author wishes here to express his indebtedness to many friends for assistance in various ways; particularly would he thank his friend and colleague—Dr. J. McCrae—for valuable help in correcting the proofs. He would also acknowledge the assistance of one of his students—Mr. Herbert Hunter—who has kindly prepared the index.

LEEDS, *March, 1902.*

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A MANUAL OF AGRICULTURAL CHEMISTRY.

TABLE OF ERRATA.

The reader is requested to kindly correct the following errors which have escaped detection until the sheets were printed:—

p. 97, line 6, *for* "27 c.c." *read* "23 c.c."

p. 99, line 7, *for* "aluminum" *read* "aluminium."

p. 173, in first line of table, *for* "soluble phosphates" *read* "mono-calcium phosphate" and make similar alterations in the 4th and 8th lines below the table.

p. 198, in the graphic formula for furfurol *delete* the H attached to the second C.

p. 341, line 13, *for* "hydrolising" *read* "hydrolysing."

AGRICULTURAL CHEMISTRY.

CHAPTER I.

INTRODUCTION.

CHEMISTRY has an intimate connection with all the operations of life, both animal and vegetable. The processes involved in vital phenomena are attended by chemical changes so complex in character that they are often difficult to unravel. Consequently it is found that while the chemical reactions occurring in most industries are thoroughly understood and can be satisfactorily explained, those attending the growth of animals and plants are, to a great extent, unknown, indeed in many cases appear to be contrary to the ordinary laws of chemistry. Thus an elementary knowledge of the science suffices in the case of many industrial operations to give a rough, superficial explanation of the chemical changes involved, whereas in studying the phenomena of life instances soon present themselves, in which reactions, of a kind altogether unexpected from an ordinary laboratory student's point of view, occur. So too in the reactions taking place in a soil it is often found that the time required is so long and the dilution of the solution so great that the direction of the change is to be attributed to mass action or other somewhat complex cause rather than to the ordinary influences governing a chemical reaction. Agricultural chemistry therefore, since it deals mainly with the changes occurring in the soil, the growth and life of plants, the feeding of animals and the preparation of food products, is frequently called upon to explain changes of the character described; a task which is often difficult and requires a knowledge of physical chemistry.

In the application of chemistry to agriculture cases often arise in which the truth of the old adage "A little knowledge is a dangerous thing" becomes strikingly apparent and the conclusions arrived at from the consideration of a particular problem from the standpoint of ordinary elementary chemistry are quite opposite to the results of actual practice. Such contradictions arise, not from any inaccuracies in general principles, but through leaving out of consideration the effects produced by some apparently insignificant circumstances or conditions.

It is evident, therefore, that although there is no distinct *agricultural* chemistry, yet the problems which arise in agriculture demand a knowledge of chemistry in which due attention is given to the peculiar circumstances under which the reactions take place.

In this work it will be assumed that the reader possesses an acquaintance with general elementary chemistry and is familiar with the properties of the more commonly occurring elements and their chief compounds.

The student of agricultural chemistry soon finds that of the seventy odd elements which are known, only a comparatively small number, some 12 or 14, are concerned in most of the changes which are brought before his notice. It may perhaps be advisable to very briefly remind the reader of the properties of these important elements, the mode of their occurrence, and the characteristics of some of their compounds. The elements which are most important to living organisms are—hydrogen, oxygen, nitrogen, carbon, sulphur, phosphorus, potassium, sodium, calcium, magnesium, iron, silicon, aluminium, chlorine, and fluorine.

Hydrogen.—This substance, as its name implies, is a constituent of water. Its most important chemical properties are its strong tendency to combine with oxygen, the act of union being accompanied by the evolution of a large amount of heat, and its power of uniting in a vast number of different proportions with carbon to form that very numerous and important group of bodies known as the hydrocarbons. It also enters into the composition of almost all compounds existing in the bodies of plants and animals, *i.e.*, into nearly all forms of organic matter. Its atomic weight is the smallest of all the elements and was formerly taken as unity, now it is more usual to take oxygen=16 as the basis of atomic weights, that of hydrogen on this scale being about 1·008. Consequently, though the proportion by weight of hydrogen in the substances comprising the crust of the earth is small, yet the number of atoms of hydrogen actually existent and taking part in the changes going on must be very large compared with those of other elements apparently (and by weight) much more abundant. Take water for example—here the hydrogen by weight constitutes only $\frac{1}{9}$ of the total and the oxygen $\frac{8}{9}$, yet there really are twice as many atoms of hydrogen as of oxygen, as indicated by the formula H_2O. In reality the relative amounts of elements present in any system so far as their chemical activity is concerned ought to be measured by the respective numbers of atoms present, not by their respective weights. Regarded in this way, hydrogen is of relatively far greater importance and abundance than is usually estimated (*v.* p. 19).

Oxygen is perhaps the most important element known. It is by far the most abundant, and takes part in a greater number of the chemical changes occurring in nature than any other element. It is, indeed, chiefly remarkable for its activity and its power of uniting with almost all other elements.

Its method of preparation and chief properties are well known to all students of chemistry, being appropriately chosen for consideration early in their course of study.

Its union with other bodies is usually attended with the evolution of much heat and often light. Present in the free state in air, it plays an important part in the chemical actions attendant upon the processes of respiration, combustion, decay, and almost all the forms of "weathering" which occur around us.

Oxidation, *i.e.*, union with oxygen, is a process of vital importance. The life of animals, especially, may be said to almost consist of oxidation. So, too, the changes occurring in the soil, the "fermenting" of hay, ensilage, &c., the putrefaction and decay of animal matter, and many other processes are largely dependent upon combination with oxygen. Union with oxygen is almost invariably accompanied by the evolution of heat, in fact to union with oxygen most artificial and many natural sources of heat (and hence of energy) owe their efficiency. The rapid combination of substances with oxygen is generally accompanied by the attainment of a high temperature and is instanced by most processes of combustion or burning. In such cases the heat evolved is rendered evident, but in others the slow combination of substances with oxygen evolves the heat so gradually that conduction and radiation are able to carry it away almost as fast as it is produced, consequently no distinct rise of temperature may be perceptible. A very important fact, and one which should always be kept in mind, is that, in all cases, the union of a given weight of a substance with oxygen evolves the same quantity of heat, however slowly or quickly the process of oxidation may take place; provided of course that the final product be the same.

It is thus possible to determine experimentally the actual quantity of heat (and thus of energy) evolved by the union of any fixed weight of various combustibles with oxygen, and the numbers so obtained will apply to all cases of burning in which these combustibles take part.

Heat is measured by the quantity of water which it can raise through 1° C. (or in some cases 1° F.). The number of units of mass (*e.g.* pounds or grammes) of water which can be raised through 1° C. by the union of the unit of mass (*i.e.* 1lb or 1 gramme) of the combustible with oxygen, is called the *heat of combustion* or the *calorific power of the substance.*

The following table gives the calorific power of a number of substances:—

Substance.	No. of grammes of water raised 1° C. in temperature by the combustion of 1 gramme of the substance.
Charcoal	8080
Hydrogen	34,460
Air-dried wood	2800
Charred wood	3600
Average coal	7500
Good coke	7050
Albumen (serum)	5918
Casein	5860

Substance.	No. of grammes of water raised 1° C. in temperature by the combustion of 1 gramme of the substance.
Albumen (egg)	5735
Muscle	5660
Peptone	5300
Asparagin	3514
Urea	2542
Fat of pig	9477
,, ,, ox	9486
,, ,, sheep	9494
,, ,, butter	9216
Olive oil	9400
Rape-seed oil	9500
Arabinose	3730
Dextrose	3740
Galactose	3720
Fructose	3755
Cane sugar	3955
Milk sugar (cryst.)	3736
,, ,, (anhyd.)	3952
Maltose (cryst.)	3722
,, (anhyd.)	3949
Cellulose	4185
Starch	4182

As has been stated, the heat of combustion of a substance is constant whatever be the manner in which union with oxygen occurs, provided only that the same final products be obtained. The temperature attained, however, varies greatly with the conditions under which combination takes place. For example the temperatures reached when substances are burnt in pure oxygen are much higher than when they burn in air, though the same products are formed and, as is seen from the above statements, the same quantities of heat are evolved in both cases. It will be easily seen why such different temperatures are yielded,—the combustion in pure oxygen takes place more rapidly, in a smaller space (generally with a smaller flame) and the process is carried on without a large amount of cool, indifferent gas (nitrogen) which would abstract heat and keep the temperature down, while in air the conditions are just the opposite.

A still more extreme case is furnished by the many processes of slow oxidation or combustion which occur so frequently in nature.

Under ordinary circumstances these processes generate heat only at about the same rate as it is carried away by contact with surrounding objects, consequently little or no elevation of temperature occurs, but occasionally the rate of loss of heat may be greatly diminished, when a decided and, in some cases, a destructive rise of temperature ensues. Under particularly favourable circumstances the loss of heat may be so small that the actual ignition point (that is the temperature at which rapid union with oxygen accompanied by flame occurs) is reached and the mass takes fire. Such cases of "spontaneous combustion" occur fairly frequently. Common causes are:—

1. Slow oxidation of drying oils, as in greasy waste in mills, &c.;
2. Fermentative changes produced by bacteria, *e.g.*, in haystacks, in the manufacture of tobacco, &c.;
3. Slow oxidation of certain minerals, *e.g.*, iron pyrites in coal;

and several others. Those of interest in agriculture will be discussed later.

Another instance of slow combustion producing only a very slight elevation of temperature is afforded by the respiratory processes of animals. Here the food acts as the combustible and the process of union with oxygen takes place by means of the blood, which absorbs the oxygen from the air in the lungs, the chief product of combustion, carbon dioxide, being carried by the blood to the lungs and there returned to the atmosphere. In this case, as in all others, the amount of heat produced is doubtless exactly proportional to the amount of the food materials oxidised, though its measurement is complicated by many other processes involving heat changes going on in the body.

Nitrogen is present in large proportion in the air, where it exists in the free state. In combination nitrogen occurs but rarely save in substances which owe their origin to animal or vegetable life. Indeed of purely mineral substances containing it we know of very few, if any. The deposits of nitrates, *e.g.*, of sodium and potassium nitrates, which are found in certain hot climates and which are largely used as sources of combined nitrogen, have almost certainly been formed by the same agencies which produce nitrates in all fertile soils—bacteria, and probably from the same sources—organic nitrogenous bodies. Unlike other elements, nitrogen appears to occur only on the outermost parts of our globe, *i.e.*, either in the atmosphere or, if underground, within a very short distance of the surface of the earth, the only noteworthy exception to this being the occurrence of coal and carboniferous shale, &c., which usually contain about 1 % combined nitrogen. It must be remembered that these deposits are of vegetable origin and were formed at the surface. The properties of free nitrogen are well known; it is a colourless, odourless gas, possessing little chemical activity, taking part in very few of the changes occurring in the atmosphere. Indeed its most remarkable characteristic is its general chemical inertness. It accompanies oxygen in all the multitudinous processes in which the latter takes such an active part and in most instances escapes unchanged. Only by very extreme means can it be caused to combine with other substances and usually heat is absorbed by the act of union.

The compounds of nitrogen, unlike the element itself, are extremely active chemically and many of them are of great importance.

All organisms, whether plant or animal, require nitrogenous compounds to build up their tissues. Compounds containing nitrogen therefore are essential ingredients in the food supply of both plants and animals. Many most powerful medicines and poisons contain nitrogen, *e.g.*, all the alkaloids—brucine ($C_{23}H_{26}N_2O_4$), strychnine ($C_{21}H_{22}N_2O$), quinine ($C_{20}H_{24}N_2O_2$), &c.—prussic acid (HCN), &c. Many nitrogen compounds are extremely unstable, *i.e.*, they readily split up into simpler compounds, the nitrogen being generally set free, thus they are often violently explosive, *e.g.*, nitro-glycerine, $C_3H_5(NO_3)_3$, gun-cotton, $C_6H_7O_2(NO_3)_3$, &c., &c.

We thus see that while free nitrogen is of comparatively little value, its compounds are of the utmost importance to all living beings. Consequently the means of utilising nitrogenous compounds and of preventing their waste, often leading to the liberation of the comparatively useless free nitrogen, are matters of intense interest and great importance. By some chemists it is thought that supplies of nitrogen compounds will fail us long before the want of phosphates, potash, or other fertilising substances becomes felt.*

It is to be hoped that by means of the nitrogen-fixing bacteria which grow in nodules upon the root hairs of certain leguminous plants, or in some other way, it may be found possible to abstract from the atmosphere sufficient nitrogen to supply the wants of both plants and animals for many centuries. Nevertheless, the rapid exhaustion of our deposits of nitrates and the enormous quantities of valuable nitrogenous materials which are allowed to run to waste in the sewage of our large cities, are serious matters for consideration as affecting the future supplies of this indispensable combined nitrogen.

Carbon is perhaps more than any of the other elements, associated with the processes of life. It constitutes a large proportion by weight of the solid portions of all animals and plants. In the mineral kingdom it is also abundant, occurring in immense quantities in carbonates, *e.g.*, those of calcium, magnesium, iron, zinc, lead, copper, &c. It also occurs in the air, in the form of carbon dioxide, the amount of which, though small relatively to the other constituents of air, is absolutely considerable and is constantly being renewed.

The properties of the three allotropic forms of carbon are fully described in any general text book of chemistry. They are not of any particular importance from our present standpoint. Much more important are the numerous compounds which carbon forms, especially with hydrogen and oxygen, and with hydrogen, oxygen, and nitrogen. Indeed it is with these compounds of carbon that almost all the chemistry of the nutrition of animals and plants is concerned, other substances taking part in vital processes (though quite essential) being small in amount.

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* Sir W. Crookes, President's address, British Association for Advancement of Science, 1898.

But although animal life and plant life are both concerned with the chemical changes of carbon compounds, yet they stand towards carbon in an essentially different aspect, for while the life of an animal eventually leads to the more or less complete oxidation of the carbon in the food consumed and the consequent production of carbon dioxide, the characteristics of a plant's vital processes are the separation of carbon from carbon dioxide and the formation of less oxidised carbon compounds.

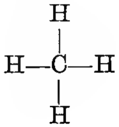
The former process is attended by the liberation of energy in the form of heat and mechanical work, the latter by an absorption and storing up of energy received in the form of light.

Carbon is remarkable for its power of uniting in a vast number of proportions with hydrogen and with hydrogen and oxygen. This power is pictured by the chemist as being due to the atoms of carbon possessing a tendency to link themselves together.

To take a simple case, there are several series of hydrocarbons known, of which the following may be taken as representatives :—

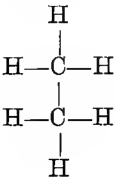
The Paraffin Series.

CH_4



$$\begin{array}{rcl} & \mathrm{H} & \\ & | & \\ \mathrm{H}- & \mathrm{C} & -\mathrm{H} \\ & | & \\ & \mathrm{H} & \end{array}$$

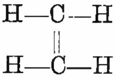
C_2H_6



$$\begin{array}{rcl} & \mathrm{H} & \\ & | & \\ \mathrm{H}- & \mathrm{C} & -\mathrm{H} \\ & | & \\ \mathrm{H}- & \mathrm{C} & -\mathrm{H} \\ & | & \\ & \mathrm{H} & \end{array}$$

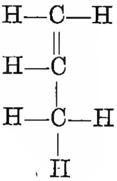
The Olefine Series.

C_2H_4



$$\begin{array}{rcl} \mathrm{H}- & \mathrm{C} & -\mathrm{H} \\ & \| & \\ \mathrm{H}- & \mathrm{C} & -\mathrm{H} \end{array}$$

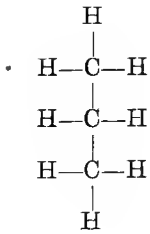
C_3H_6



$$\begin{array}{rcl} \mathrm{H}- & \mathrm{C} & -\mathrm{H} \\ & \| & \\ \mathrm{H}- & \mathrm{C} & \\ & | & \\ \mathrm{H}- & \mathrm{C} & -\mathrm{H} \\ & | & \\ & \mathrm{H} & \end{array}$$

The Paraffin Series.

C_3H_8

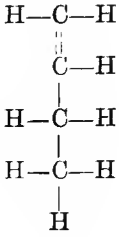


$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ & & H & & \end{array}$$

&c.

The Olefine Series.

C_4H_8



$$\begin{array}{ccccc} H & - & C & - & H \\ & & \| & & \\ & & C & - & H \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ & & H & & \end{array}$$

&c.

In each of these two series it will be observed that every member differs from the one preceding it by CH_2 and its graphical formula is written by simply adding a carbon atom attached to two hydrogen atoms between the terminal groups in the chain. A similar power of linking together is shown by the carbon atoms in other carbon compounds. It will be noted from the examples given that the linkage of two carbon atoms together may be by one or two of their combining affinities.

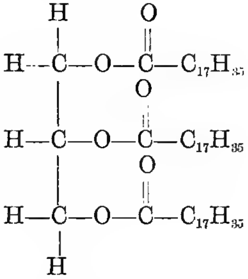
The presence of one pair of doubly linked carbon atoms is the characteristic of the olefine series. In another series, the acetylene, trebly linked carbon atoms occur, *e.g.*, $HC\equiv CH$, acetylene itself. It is to this power of the carbon atoms of linking themselves together that the possibility of the existence of such an immense number of carbon compounds is due. No other element shows the same power, unless it be silicon, a few compounds of which of the above type have been prepared.

In consequence of this unique property of carbon it is now customary to place the study of carbon compounds in a separate division of chemistry. To this branch of knowledge the name of *organic chemistry* has been given, and although it is of comparatively recent growth it has already attained vast dimensions.

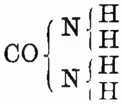
A very large number of the compounds present in the bodies of plants and animals are made up of compounds of the four elements just described. Among these compounds the following are important:—

1. *Carbohydrates*, *e.g.*, starch and cellulose, $C_6H_{10}O_5$, grape sugar, $C_6H_{12}O_6$, cane sugar, $C_{12}H_{22}O_{11}$, &c.
2. *Organic acids*, *e.g.*, acetic acid, $CH_3.COOH$, oxalic acid, $C_2H_2O_4$, &c.
3. *Fats*, essentially salts of glyceryl, C_3H_5, combined with a fatty acid, *e.g.*, stearic acid, $HC_{18}H_{35}O_2$, oleic acid, $HC_{18}H_{33}O_2$, &c. These glyceryl salts, or glycerides as they are sometimes called, are possessed of a constitution similar to the following, which represents glyceryl stearate (glyceride of stearic acid, or "stearine").

$$C_3H_5\ (C_{18}H_{35}O_2)_3$$

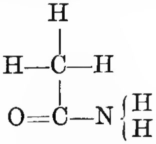


4. *Hydrocarbons*, *e.g.*, turpentine, $C_{10}H_{16}$.
5. *Albuminoids*, containing all four of the elements in question associated with small quantities of sulphur and phosphorus. The constitution of these substances is not understood. They always contain about 16% of nitrogen.
6. *Amides*.—These also are compounds of carbon, hydrogen, oxygen, and nitrogen, but their structure is much less complex than that of the albuminoids. A large number have been prepared, the characteristic feature being that they contain the group NH_2 united with an oxygen-containing compound of carbon; *e.g.*, urea is an amide, $CO(NH_2)_2$.



$$\mathrm{CO}\left\{\begin{array}{l}\mathrm{N}\left\{\begin{array}{l}\mathrm{H}\\ \mathrm{H}\end{array}\right.\\ \mathrm{N}\left\{\begin{array}{l}\mathrm{H}\\ \mathrm{H}\end{array}\right.\end{array}\right.$$

Amides may be regarded as being organic acids in which the OH groups have been replaced by NH_2. A simpler amide than the above is acetamide, $C_2H_3O.NH_2$, or



These compounds will be discussed at greater length hereafter.

Sulphur.—The occurrence and properties of this element are well known and need not be discussed here. In the nutrition of plants and animals it plays a small part, but still it is essential.

It occurs in small quantity in albuminoids and, in certain plants, in the form of sulphides and sulphocyanides of organic bases. In animals it is particularly abundant in the hair or wool.

Plants probably obtain the sulphur they require from the sulphates present in the soil, and in most cases from calcium sulphate. It is to be noted that soluble metallic sulphides are violent plant poisons, as are many other unoxidised sulphur compounds (*e.g.*, sulphocyanides, sometimes present in commercial sulphate of ammonia). Yet it is found that certain plants actually secrete sulphides and sulphocyanides of organic bases and owe their characteristic odour or flavour to the presence of these compounds. Such is the case with mustard, garlic, and many other plants.

Phosphorus.—The properties of this element are very remarkable and are well known to all students of chemistry. In agriculture its compounds, the various salts of phosphoric acid, are of the utmost importance.

Phosphorus is extremely widely distributed, though generally in small quantities. It is present in almost every mineral and rock, though the average amount present in the soils and rocks of the earth's crust probably does not exceed one or two parts in 10,000. From the soil plants obtain their phosphates; these in turn pass into the bodies of animals, where they often accumulate in large quantities, thus the bones or shells of animals always contain relatively large amounts of phosphate of lime.

Some minerals, too, consist mainly of phosphates, *e.g.*, *apatite* consists of $3Ca_3P_2O_8.CaCl_2$ or $3Ca_3P_2O_8.CaF_2$; *vivianite* is essentially $Fe_3P_2O_8 8H_2O$. More abundant are deposits of impure phosphate of lime in the various forms of *phosphorite*, *osteolite*, *coprolites*, &c., &c. These are often used as fertilisers.

Potassium occurs in many silicates: some contain a relatively small quantity, while in others, *e.g.*, *orthoclase* or *potash felspar*, $Al_2O_3.K_2O.6SiO_2$, the proportion of this element is considerable. It also occurs largely in sea-water, from which sea-weeds often accumulate large quantities of potassium compounds. Another very important source of potassium is the huge saline deposit at Stassfurth; this is supposed to be the result of the evaporation of a large inland sea, and consists mainly of sulphates and chlorides of magnesium, potassium, sodium, and calcium. This deposit has been extensively worked for some years, largely for supplies of potash salts for agricultural purposes. The element itself is of little interest from an agricultural standpoint, as its great affinity for oxygen and other electro-negative elements renders its preparation and preservation difficult. Its compounds, however, are of the utmost importance, indeed potash seems very intimately connected with the processes of plant growth and is always most abundant in the growing portions, the young shoots or twigs. The maintenance of a supply of its compounds is essential to a plant's welfare. In the plant it is combined with various acids—nitric, sulphuric, hydrochloric, and very often with organic acids, *e.g.*, oxalic, malic, citric, or tartaric. In the ashes of plants it is usually found as carbonate, this being formed by the destruction of the organic potassium salts by heat. The ashes of the twigs and leaves of trees, indeed, formerly furnished almost the whole of the potash used in the arts. The earlier chemists distinguished potash by calling it the "vegetable alkali" in contradistinction to the "mineral alkali," by which they meant soda, and the "volatile alkali" or ammonia.

Potash compounds are remarkable in the property which they possess of being retained by clay, and especially by the mixture of clay and organic matter found in nearly all fertile soils. In this respect potash differs greatly from soda, for whose compounds soil possesses little or no retentive power. This retention of potash by soil probably explains the fact that in sea-water there is so much more of sodium compounds than of potassium ones, notwithstanding the fact that the primary rocks of the earth's crust contain about equal amounts of these substances. Denudation carries off to the sea large quantities of soluble sodium compounds, but comparatively little potassium salts, owing to their retention by the clay, &c., simultaneously formed by the processes of decay of the felspar, mica, &c.

Sodium occurs in many silicates, replacing potash. It is extremely widely diffused throughout nature and in the form of common salt plays an important part in animal nutrition. It is asserted by many authorities to be a merely accidental constituent of plants, and in most instances it is found that the exclusion of sodium from a plant's food produces no ill effects; on the other hand, many marine plants and plants growing near the coast contain large quantities of sodium compounds and a due supply appears essential to their welfare. Although sodium is chemically very like potassium, forming compounds whose properties are very similar to those of that element, its compounds are not retained by the clay or organic matter of a soil, and if applied to the land soon find their way into the drains and thence by streams and rivers to the sea.

Certain sodium salts are used in agriculture, *e.g.*, sodium nitrate and sodium borate, but in all cases it is the acid constituent which is of most value, and rarely that the sodium itself plays any important part, unless it be in rendering more available the potash or other valuable constituents of the soil.

Calcium is an extremely abundant element, always occurring in combination. The carbonate, constituting the main ingredient in *limestone*, *chalk*, and *marble*, and the sulphate, which is found as *gypsum* or *selenite*, $CaSO_4.2H_2O$, and also as *anhydrite*, $CaSO_4$, are very abundant. Calcium is also found in union with phosphoric acid in the various deposits of *apatite*, $3[Ca_3P_2O_8]CaCl_2$ (or CaF_2). Calcium carbonate, which is extremely abundant, dissolves in water containing carbonic acid and is therefore found in all natural waters, from which it is extracted by shell-fish, &c., and forms the chief constituent of their hard parts. It is essential as a plant food, but its agricultural importance arises rather from its effect in altering the texture of soils and in modifying the chemical changes attending the fermentation and decay of their organic matter. For example, calcium carbonate, lime, and other calcium compounds have a remarkable action upon clay, rendering it much less tenacious and plastic. The presence of calcium carbonate or some other substance capable of acting as a weak base is essential to the important process of nitrification. Into plants calcium is probably absorbed in the form of nitrate, phosphate, sulphate, or carbonate, and is found in all parts of the organism. In animals the calcium compounds are usually concentrated largely in the hard parts, the bones or shells.

Owing to its abundance, calcium is rarely used as a manure in the strict sense of the word, *i.e.*, as a plant food, but it is largely used in agriculture either for the sake of the improvements it produces in the texture of the soil as free lime or in combination with other ingredients of manurial value, *e.g.*, phosphoric acid, as basic slag, superphosphates, &c.

Magnesium also occurs only in a state of combination, often associated with calcium. Limestone and other forms of carbonate of lime invariably contain some carbonate of magnesium, which in some, *e.g.*, *magnesian limestone*, is present in considerable proportion.

Magnesium is also found in many silicates, *e.g.*, *meerschaum*, *steatite*, *talc*, and *serpentine*. It is also present in sea-water and in many mineral springs, to which it imparts a bitter taste.

Large quantities of magnesium compound are found associated with potassium compounds in the Stassfurth deposits.

Magnesium is always present in plants, but as a rule there is far more present in a soil than is necessary for the crops' requirements. Consequently it is not of much importance as a fertiliser.

Iron is very abundant in nature, generally in the state of combination. Native metallic iron is occasionally found, but in insignificant amount. As oxides (Fe_2O_3 and Fe_3O_4) and carbonate ($FeCO_3$) immense quantities occur in the minerals known respectively as *hæmatite*, *magnetite*, and *spathic iron ore*. These compounds form the most valuable ores of iron. In combination with other substances iron is also abundant. It is the main cause of the red or yellow colour of soils. Two series of compounds are known, ferrous salts, in which iron is divalent, and ferric compounds, in which it is trivalent; only the latter are suited to the requirements of plants.

Iron is essential as a plant food, but a very small quantity suffices. It is rarely advisable, therefore, to use iron compounds as manures.

Manganese resembles iron in most of its properties. It is always found in union with other elements, often with oxygen, *e.g.*, as *pyrolusite*, MnO_2, *psilomelane*, $BaO.\ 2MnO_2$. It is apparently not essential as a plant food, but is often found in the ashes of plants.

Aluminium is never found in the free state in nature. It is extremely abundant and is one of the most important constituents of most mineral silicates. In the form of *felspar* and *mica*, it enters largely into the composition of many igneous rocks. By the action of water and carbon dioxide upon felspar ($K_2O.Al_2O_3.6SiO_2$) the potash is to a great extent removed and a residue of *kaolin* or *china clay*, $Al_2O_3.2SiO_2.2H_2O$, is eventually obtained. Ordinary clay consists of a mixture of kaolin with some incompletely decomposed felspar and therefore is rich in potash. Clay constitutes an important ingredient of soils, to which it imparts valuable properties, especially as regards retentive power for water and other substances.

Aluminium is apparently not a plant food, though the ashes of some few plants contain it in small quantities.

Silicon always occurs in combination, either with oxygen as silica, SiO_2, which is found as *quartz*, *flint*, *sand*, &c., or with oxygen and metals as the very numerous and abundant silicates, *e.g.*, felspar, mica, &c., &c.

Sand, which consists of little fragments of quartz, is very permanent and is little affected by water or carbon dioxide.

Sand forms the largest portion of most soils and, if pure quartz, is devoid of plant food. It greatly affects the porosity and general texture of the soil. The silica which many plants contain is not believed to be essential to their growth; it probably is taken in by the roots of the plant in the form of soluble silicates or the soluble silica formed, not from the sand itself, but by the decomposition of silicates.

Titanium, which resembles silicon in its chemical functions, is not nearly so abundant. Its presence in the plant is usually overlooked, though according to Wait* it is almost invariably present in plant ash.

Chlorine is an element possessed of remarkable and well-known properties. It rarely occurs in the free state in nature, but in the form of metallic chlorides is very abundant. This is particularly true of sodium chloride, NaCl, which is found in sea and most spring water and as *rock-salt.* Chlorine is an essential constituent of plants, and in some crops, *e.g.*, mangels, it occurs in large quantity.

Fluorine occurs mainly as calcium fluoride, CaF_2, in the mineral known as *fluor-spar*. It is also present in almost all naturally occurring forms of calcium phosphate, and doubtless, in quantities too small to be readily detected, in many other minerals. The element itself is difficult to prepare owing to its great chemical activity.

It is found in combination in the bones, blood, and urine of animals. Bone-ash contains about 4 % of calcium fluoride, while many mineral phosphates contain as much as 7 or 8 %. According to Lorenz[*], the evolution of hydrofluoric acid by a phosphate on treatment with sulphuric acid may be taken as a proof that a mineral phosphate is present. This test is not entirely satisfactory, since many mineral phosphates do not give it, indeed they are known to contain practically no fluoride, but chloride. Thus, there are two varieties of apatite corresponding to the formulæ $3Ca_3P_2O_8.CaF_2$ and $3Ca_3P_2O_8.CaCl_2$, and many specimens have a composition intermediate between those expressed by the above formulæ. Of course the chloride variety is preferable for the manufacture of superphosphate.

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* Jour. Amer. Chem. Soc., 1896, 18, 402.

Boron always occurs in combination as boric acid (HBO_2 or H_3BO_3) or borates. It is not a very abundant element except in a few localities, *e.g.*, in Tuscany and in California, but of recent years its presence in a number of plants and products from plants, particularly in wines[†] and the leaves, stalks, &c., of the vine[‡] has been detected by various observers, leading to the conclusion that boric acid must be present in soils, which probably derive it from igneous rocks.

There is no evidence that it is essential to plant life. Boric acid or boracic acid is possessed of considerable anti-putrefactive properties and is often used for preserving milk and other food products.

Relative Abundance of the Elements.—F. W. Clarke,[§] of the U.S.A. Geological Survey, has estimated very carefully the relative proportions of the more common elements constituting the earth's crust to a depth of ten miles from the surface. He estimates that of this—

93 % is composed of solid rock, &c.
7 % ,, ,, water and air

—the latter only amounting to about ·03 %.

The following table gives the relative abundance by weight of the elements named :—

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[*] Jour. Soc. Chem. Ind. 1889, 307.

[†] Crampton, Amer. Chem. Jour., 11, 227.

[‡] Baumert, Ber. 21, 3290.

[§] Bull. Philos. Soc. Washington, xi., 227.

		Solid crust 93 %.	Ocean 7 %.	Mean including air.
1.	Oxygen ...	47·29	85·79	49·98
2.	Silicon ...	27·21	—	25·30
3.	Aluminium ...	7·81	—	7·26
4.	Iron ...	5·46	—	5·08
5.	Calcium ...	3·77	0·05	3·51
6.	Magnesium ...	2·68	0·14	2·50
7.	Sodium ...	2·36	1·14	2·28
8.	Potassium ...	2·40	0·04	2·23
9.	Hydrogen ...	0·21	10·67	0·94
10.	Titanium ...	0·33	—	0·30
11.	Carbon ...	0·22	0·002	0·21
12.	Chlorine ...	0·01	2·07	0·15
13.	Phosphorus ...	0·10	—	0·09
14.	Manganese ...	0·08	—	0·07
15.	Sulphur ...	0·03	0·09	0·04
16.	Barium ...	0·03	—	0·03
17.	Nitrogen ...	—	—	0·02
18.	Fluorine ...	0·02	—	0·02
19.	Chromium ...	0·01	—	0·01

These numbers, it must be remembered, are merely estimated, and can only claim to be approximations. They have been deduced from many analyses of rocks, but our acquaintance with the distribution and relative abundance of these rocks must obviously be incomplete.

The above table, however, giving as it does the proportions *by weight* of the elements, does not really represent their relative abundance reckoned in atoms. This latter certainly appears to the author to be the more correct way of grading their importance. In order to find the relative number of atoms it is only necessary to divide the numbers in the above table by the respective atomic weights. In this way the following table has been calculated, giving the number of atoms of each element present in a total of 100,000 atoms.

Table showing the relative *numbers of atoms* of the elements present in the earth's crust to a depth of 10 miles, including the ocean and the atmosphere :—

1.	Oxygen	54,684
2.	Hydrogen	16,455
3.	Silicon	15,818
4.	Aluminium	4707
5.	Magnesium	1822
6.	Sodium	1735
7.	Iron	1588
8.	Calcium	1537
9.	Potassium	1001
10.	Carbon	324
11.	Titanium	110
12.	Chlorine	68
13.	Phosphorus	51
14.	Manganese	26
15.	Nitrogen	25
16.	Sulphur	23
17.	Fluorine	17
18.	Barium	4
19.	Chromium	4
		100,000

The great changes in the order of hydrogen (from 9th to 2nd place), sodium (7th to 6th), iron (4th to 7th), and calcium (5th to 8th) will be noted. The low position of nitrogen, which is usually regarded as so abundant, in both tables is also worthy of attention. It is hardly necessary to say that the other elements are very much less abundant and have been ignored in the compiling of the above tables.

CHAPTER II.

THE ATMOSPHERE.

ALMOST all the vital phenomena important from an agricultural aspect occur in contact with and largely by the action of the air around. Moreover, air plays an important part in the formation of soils and profoundly affects the temperature and climate of the earth. It is therefore obvious that a knowledge of the composition and properties of the atmosphere is absolutely essential in order that the chemistry of the processes involved in the life of animals and plants may be clearly understood.

The reader will already possess some acquaintance with the chemical nature of atmospheric air and with the properties of its chief constituents.

In this chapter, therefore, is given only a short summary of what is known of the extent, variations in composition, and functions of the constituents of air.

With reference to the *extent*, it is found that air exerts an average pressure of about 14·75lb. per sq. in. (1033 grammes per sq. cm.) at the sea-level. This pressure is due to the earth's attraction for the air above and is, of course, a direct measure of the weight of the atmosphere. There rests, therefore, on every square foot of surface 14·75 × 144lb. of air; or upon an acre the total weight of air would be 41,300 tons. Allowing for the space occupied by land above the sea-level, Herschel has calculated that the mass of the atmosphere is about $\frac{1}{1200000}$ of that of the earth.

Although it is possible, as shown above, to estimate fairly accurately the weight of the atmosphere, there is very little information available from which the height to which the atmosphere extends can be calculated.

It can easily be shown that if the atmosphere were homogeneous its height would be between 5 and 6 miles; but, as is well known, the density rapidly diminishes with the height above the sea-level. At a height of 5520 metres (*i.e.*, about 18,110ft.) the pressure is half what it is at the sea-level, while at 11,040 metres (or 36,220ft.) it is reduced to one-fourth of the sea-level pressure, and so on. In the case of small elevations it may be said that, roughly, an ascent of 900ft. lowers the barometric pressure by an inch. From observations on luminous meteorites and refraction of sunlight it has been estimated that at a height of 200 miles air has a very small but appreciable density. It is almost impossible to conceive of an actual, defined limit to a gaseous atmosphere.

The pressure of the atmosphere varies, as is well known, from day to day, and upon the variations of pressure the direction and force of the wind depend.

From a consideration of the mean pressures of many different parts of the world it has been discovered that there are two broad belts of high pressure, one north and the other south, running roughly parallel to the equator. Near the equator itself, and also near the poles, are regions of low mean pressure.

Another fact in connection with atmospheric pressure has been clearly noticed, most distinctly in tropical districts—a diurnal variation, there being two maxima, often about 9 a.m. and 9 p.m., and two minima about 3 a.m. and 3 p.m. So regular is this variation in some hot countries that, according to Humboldt, it is almost possible to tell the time of day by reading the barometer.

The consideration of the relative heights of the barometer obtaining at different places at a given time affords one of the most important criteria in forecasting weather.

Though this subject to the farmer is obviously of the greatest importance, and though considerable progress has recently been made in connection with it, this is not the place in which it can suitably be discussed. The reader should consult a modern treatise on meteorology.

Dry air is almost diathermanous, *i.e.*, transparent to heat rays. Consequently it allows the sun's heat to pass through with but little loss, becoming only very slightly warmed. It also allows a considerable, though probably much less, percentage of the heat radiated from the earth to pass through it.

If, however, any appreciable amount of aqueous vapour or suspended solid matter be present, both forms of radiant heat are to a large extent absorbed. The presence of clouds confers a still greater retentive power for heat. This effect of aqueous vapour or of clouds is often very apparent at night; it is a matter of common experience that clear starlight or moonlight nights, even in summer, are often cold, because of the free radiation of heat from the earth into space, while cloudy nights are generally much warmer. Water in the air, too, has an important effect in conveying heat from one place to another. Whenever water becomes gaseous, heat is absorbed, and when the vapour condenses again (often in the upper regions of the air) heat is evolved.

Air itself is thus little affected by the direct heat of the sun, being heated either by contact with the hot surface of the ground or by the aid of its own aqueous vapour.

The specific heat of air is about ·24, that of water being unity, *i.e.*, to raise the temperature of a given weight of air through a given interval of temperature requires only about one-fourth as much heat as would raise the temperature of the same weight (or about $\frac{1}{800}$ of the volume) of water through the same interval cf temperature. It is thus evident that by cooling a given volume of warm water through one degree (or any fixed interval of temperature) enough heat is extracted to raise the temperature of about 3200 volumes of air by the same amount.

Hence the potency of currents of warm water, *e.g.*, the Gulf Stream, in affecting climate and the slowness with which water is cooled and converted into ice by cold winds, &c.

The mean temperature of the atmosphere varies greatly, one important factor being the latitude, which mainly determines the amount of heat received from the sun. The temperature is also found to vary greatly along the same parallel of latitude with the nature of the soil and particularly with the proximity or otherwise of large areas of water, places near the sea-coast always enjoying a more uniform climate than those far inland. Then, too, the height above the sea-level greatly affects the temperature of a place, there being on the average a fall of 1° C. for about every 400ft. above the sea-level but the rate is very variable.

COMPOSITION OF THE ATMOSPHERE.

Air is a mechanical mixture of various gases and vapours, but it invariably contains suspended solid matter, some of which consists of micro-organisms.

The main gaseous constituents are—oxygen, nitrogen, argon, carbon dioxide, water vapour, ammonia, oxides of nitrogen or nitric acid vapour, and ozone. All these are subject to variation, but to very different extents.

Nitrogen, the largest constituent, is the least variable in amount. It usually constitutes about 78% by volume or 75·5% by weight of dry air. Its function in the atmosphere has usually been regarded as mainly that of a diluent. Apparently very few reactions take place in the atmosphere in which nitrogen takes part. Recently, however, many obscure changes in which the free nitrogen of the air enters into combination with oxygen and hydrogen have been observed, some of which are of the greatest importance in agriculture. These changes occur by the agency of micro-organisms in the soil or plant (*v.* Chap. IV.).

Very high temperatures, such as obtain in the blast furnace, will cause nitrogen to combine with carbon in the presence of alkalies with the production of cyanides. Nitrogen may be made to combine with oxygen under the influence of the high temperature of the electric spark,* and such combination is doubtless brought about in the atmosphere by lightning discharges, with the production of oxides of nitrogen and eventually of nitric acid. Similar combination between nitrogen and oxygen has been observed to occur during the combustion, in air, of certain substances which in their burning produce a high temperature.

The amount of free nitrogen removed from the atmosphere by these various agencies is relatively small and probably quite equalled by that yielded by processes of decay and putrefaction.

It is found that organic nitrogenous bodies during decomposition yield their nitrogen, partly as ammonia and, under certain circumstances, partly as free nitrogen. So, too, by combustion, organic substances evolve practically the whole of their nitrogen in the free state.

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* McDougal and Howles (J.C.S., 1900, abst. ii., 651). found that by a large electric discharge in air, as much as 303 grammes of nitric acid per 12 horse-power-hours could be produced.

Oxygen, the most important constituent, since it takes part in so many of the reactions occurring in the atmosphere, is liable to considerable local variations. Its amount, on the average, is nearly 21% by volume or 23·2% by weight of dry air. As processes of oxidation are taking place so continually it might be expected that the proportion of oxygen in air would show great variations from place to place. In consequence, however, of diffusion, air currents, and the compensating influences of vegetation, the variations which have been observed, though well marked, are not great.

The extremes noticed by various observers are:—

Bunsen	...	20·84	—	20·97
Regnault	...	20·90	—	21·00
Angus Smith	...	20·89	—	21·00
Leeds	...	20·82	—	21·03
Jolly ...	...	20·53	—	21·01

As is to be expected, the air of towns is found to contain less oxygen than that of the country or over the sea. The lower numbers given in the above table were, in all cases, observed in the air of large cities. In marshy places, too, the amount of oxygen is generally lower than elsewhere.

Comparatively few experiments on the composition of air from great heights have been made, but the general result of what is known is in agreement with theory, which indicates that relatively less of the heavy constituent, oxygen, should be present in such air.* In the Alps it has been observed that a

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* According to Hinrichs (Compt. Rend., 1900, 131, 442), if each constituent of the air were independent of the others the composition of air at various heights would be as given in the accompanying table.

Altitude in kilometres.	Carbon dioxide.	Oxygen.	Argon.	Nitrogen.	Hydrogen.
0	·03	21·00	1·20	77·75	0·02
10 (= 6·214 miles)	·02	18·43	0·75	80·74	0·06
20	·01	16·97	0·46	83·26	0·20
30	·00	13·90	0·28	85·18	0·64
40	—	11·86	0·16	85·94	2·04
50	—	9·83	0·12	83·94	6·11
60	—	7·52	0·00	75·54	16·94
70	—	4·7	—	56·2	39·1
80	—	2·2	—	31·0	66·8
00	—	0·7	—	12·9	86·4
100 (= 62·14 miles)	—	0·3	—	4·6	95·1

From the above table it is seen that the carbon dioxide becomes inappreciably descending current of air produces a lower proportion, while an ascending wind gives a higher proportion of oxygen.[*] Differences of ·18% (by weight) were observed on two consecutive days at a height of 2060 metres. In Paris the same author gives 23·20% as the mean proportion of oxygen by weight, while 23.1% by weight is the amount he estimates as the average in London air.

In 1886 a series of daily analyses of air were made simultaneously at Dresden, Bonn (Germany), Cleveland (U.S.A.), Para (Brazil), and Tromsöe (Norway), from April 1st to May 16th. The mean values for the amount of oxygen were :—

Para	20·92 %,	by volume
Bonn	20·92 ,,	,,
Cleveland	20·93 ,,	,,
Dresden	20·93 ,,	,,
Tromsöe	20·95 ,,	,,

The maximum was 21·0 at Tromsöe and the minimum 20·86 at Para. The mean percentage of oxygen of the whole series was 20·93.[†]

Argon was discovered in 1894 by Lord Rayleigh and Prof. Ramsay. The experiments which led to its discovery were the determinations of the densities of gases, in which it was noticed that nitrogen prepared by the removal of oxygen and carbon dioxide from atmospheric air was distinctly heavier than nitrogen prepared from chemical compounds. This fact was eventually traced to the presence, in air, of a hitherto unknown substance, which was named *argon* by the discoverers.

Argon is a gas possessed apparently of no chemical proper-

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small at a height of 30 kilometres (about 18·6 miles), that the proportion of nitrogen attains a maximum at about 40 kilometres (about 25 miles), that at a height of about 60 kilometres (37 miles) the oxygen and hydrogen are in the proportion in which they combine with explosion to form water. Explosion in this highly rarefied atmosphere would be impossible, especially in the presence of so large a quantity of nitrogen.

Hinrichs asks—might not the hydrogen found in meteoric iron be obtained during the passage of the meteorite through the outermost layers of our atmosphere, which, according to the table, consists of almost pure hydrogen? It may be mentioned that hydrogen is, according to Gautier (Compt. Rend., 1898, 127, 693), always to be detected in pure air, in proportion varying from 11 to 18 per 100,000, *i.e.*, ·01 to ·018 % by volume. Moreover, he has shown that hydrogen is to be found among the gases evolved by the action of water upon many rocks, *e.g.*, granite, at a temperature of about 280° or 300° (Compt. Rend., 1900, 647). In a later paper, however, doubt is expressed as to the hydrogen being actually derived from the granite.

[*] Leduc, Comp. Rend., 1898, 413.

[†] Hempel, Ber., 20, 1864.

ties whatever, that is, it appears to be incapable of uniting with any other substance or even with itself, for unlike most gases, its molecule contains only one atom. Its density when carefully purified was found to be 19·957, which gives as its atomic (and molecular) weight the number 39·914. So far as is known argon takes part in none of the chemical changes which occur in the atmosphere.

Associated with argon, Ramsay has found several other gases of the same inert character and monatomic molecules, but differing in density and other physical properties. These have been named *helium* (identical with the substance so named, which was, long ago, detected in the sun by spectroscopic analysis), density 2·0; *neon*, density 10·0; *krypton*, density 22·5; and *xenon*, density probably about 40—41. These elements, however, are present in such extremely small quantities and their chemical inertness is so great that they are probably of no importance from our present standpoint.

The amount of argon present in the air is apparently very constant—about ·94 % by volume or 1·3 % by weight. It constitutes about 1·19 % by volume of the residue left after the removal of oxygen.

Carbon Dioxide.—This constituent, though present only in small proportion (usually less than ·04 % by volume), is of great importance with reference to vegetable life. Its amount is subject to considerable variation since it is a constant product, in large quantity, of the combustion and putrefaction of all organic bodies.

In the free open country, air contains on the average about ·033 % of carbon dioxide.[*] In large towns or in the neighbourhood of manufactories the quantity is usually larger. In London, Angus Smith found ·044, in Glasgow ·05, in Manchester ·045. The amount is always greater during fogs (sometimes rising to ·1 %) and snow.

Air in the country shows a distinct diurnal variation, the amount of carbon dioxide being greater at night. Armstrong's[†] experiments made at Grasmere in summer-time gave ·0296 %

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[*] Recent determinations have almost invariably given lower values for the mean amount in the atmosphere.

[†] Pro. Roy. Soc. 1880, 343.

for the day and ·0330 % for the night, and similar results have been obtained by other observers. Müntz and Aubin give ·0278 % as the universal average; they noticed ·0273 as the mean in the day and ·0288 in the night.* H. T. Brown gives as a result of many determinations made in 1898-99, ·0285 as the mean and ·027 and ·030 as the usual limits of variation in summer.† Over the sea or in places far from vegetation no such difference can be detected, and the average amount (·030 %) is lower. Schulze, as a mean of nearly three years' daily determinations of carbon dioxide in the air at Rostock, found ·0292 %, the maximum being ·0344 % and the minimum ·0225 %.‡

Theoretically, assuming that the composition of the atmosphere is not modified by any disturbing influences, the amount of carbon dioxide should diminish with the height above the sea-level. Experimental evidence on this point is conflicting. Truchot found distinctly less at heights of 1440 (·020 %) and 1880 metres (·0172 %) than nearer the sea-level (·0313), while recently (1899) Thierry§ found on Mont Blanc ·0262 % at 1080 metres and ·0269 % at 3050 metres. Müntz and Aubin‖ found in 1882, as a mean of many analyses, ·0286 volumes on the Pic du Midi (2877 metres), practically the same as in the plains. The earlier observers, too, found more on the tops of mountains than at sea-level. It is obvious that vegetation must have a great local influence on the amount of carbon dioxide and may, in some cases, cause misleading indications.

Among the many causes tending to increase the amount of carbon dioxide in the air, the following are the most important:—

1. Emission from volcanoes, deep springs, and other subterranean sources; immense quantities are thus sent into the atmosphere.
2. Oxidation of carbonaceous matter; this occurs in the processes of respiration of animals and plants, the decay and fermentation of animal and vegetable products, and the combustion of most fuels.

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* Bieder. Central. 1883, 469.

† Brit. Assn. Report, 1899, Presidential address, section B.

‡ Versuch. Stat. 14, 366.

§ Compt. Rend. 129, 315.

‖ Compt. Rend. 93, 797.

3. The dissociation of carbonates by heat; this is seen in such processes as lime-burning.
4. The decomposition of calcium bicarbonate by shell-fish, the calcium carbonate being retained in building up the shell, and the carbon dioxide evolved.

The main cause tending to diminish its quantity is the decomposition effected by the green portions of plants under the influence of light. The rapidity with which this absorption of carbon dioxide occurs is astonishing (*v.* Chap. IX.). Other causes which remove it are the weathering of rocks, *e.g.*, the conversion of felspar into kaolin—

$$Al_2O_3.K_2O.6SiO_2+CO_2+10H_2O=Al_2O_3.2SiO_2.2H_2O+K_2CO_3 +4H_4SiO_4.$$

—and the conversion of normal into acid carbonates. Indeed, to this last-mentioned action and its reverse, in the case of calcium carbonate in sea water, Schloesing attributes the maintenance of the constancy of composition of the atmosphere above the ocean. If, from any cause, the quantity of carbon dioxide in the air above the ocean increases, an increased amount goes into solution as calcium bicarbonate, whereas if the quantity in the air diminishes a portion of the dissolved bicarbonate dissociates, thus liberating some of the gas.

Ammonia is a small but important constituent. It exists, probably, as carbonate, nitrite, and nitrate in the air. Its amount is very variable and is always greater in town than in country air.

Truchot in 1874 found ·93 to 2·79 milligrams of ammonia in 1 cubic metre of air collected in Auvergne at a height of 395 metres above the sea, on the Puy de Dome (1446 metres) he found 3·18 milligrams, and on the Pic du Saucy (1884 metres) 5·5 milligrams per cubic metre. He concludes that the amount of ammonia increases with the elevation and is greater in cloudy than in clear weather.* These amounts are much greater than have been found by other observers, and his conclusions as to distribution of the ammonia are not generally accepted. Levy at Montsouris† found as a mean 1·68 milligrams of ammonia in 100 cubic metres of air, in winter; and 2·09 milligrams per 100 cubic metres in summer. The maximum observed was 9 milligrams per 100 cubic metres, while on several occasions no ammonia was present. According to Heinrich* air contains the greatest amount of ammonia in June, the least in February. He found three times as much in the summer months as in the winter, while spring and autumn gave intermediate values.

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* J.C.S. 1874, abstracts, 223.

† J.C.S. 1877, 509; 1878, 243, and 1880, 848.

Ammonia, in common with nitric acid and suspended matter, is found in rain-water.

According to Levy rain (unlike air) in summer contains least and in winter most ammonia. This may be due to the solubility of ammonia being greater in cold than in hot water. At Montsouris† the following were the mean amounts of ammonia per litre, rainfall (in m.m.), and quantity of nitrogen (ammoniacal) falling upon each square metre in each of the following years:—

		Rainfall.	Ammonia.	Nitrogen per sq. met.
1875-76	...	541·5 m.m.	1·98 mgm.	1·074 grm.
1876-77	...	601·7 ,,	1·54 ,,	·929 ,,
1877-78	...	600·1 ,,	1·91 ,,	1·149 ,,
1878-79	...	655·3 ,,	1·20 ,,	·787 ,,

—This, being practically town rain, is richer in ammonia than rain falling in country places. As the average of 16 years' observations Levy gives 2·2pts. per million of ammonia = 1·82pts. N. per million in the rain at Montsouris. (See also analyses of rain-water p. 31.)

Bunsen observed that at the commencement of a shower the rain contained 3·7 milligrams of ammonia per litre, while at the end only ·64 milligrams were present.

Nitric Acid, or some compound of nitrogen and oxygen, is also found in air, in which it probably exists in the form of nitrate and nitrite of ammonia, and according to Müntz and Aubin‡ these in the state of finely-divided solid. The authors quoted state that thunderstorms (and the accompanying formation of nitrates) are confined to the lower portion of the atmosphere, below 3000 metres, and that above that height no nitrates are found in rain or snow.

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* J.C.S. 1898, abst. ii. 3, 114. † Compt. Rend. 91, 94. ‡ Compt. Rend. 95, 919.

The amount of nitric acid in air is so small that it can only be detected, as a rule, by examination of rain-water, in which it becomes more concentrated.

Rain-water, too, brings down ammonia and suspended matter, so that analyses of rain-water are valuable as indications of the composition of the atmosphere. Many such analyses have been published. Thus Angus Smith* in 1872 gave the following as the result of a large number of analyses:—

ANALYSES OF RAIN-WATER.

PARTS PER MILLION.

Where collected.	Hydrochloric acid.	Sulphuric acid.	H_2SO_4 for 100 HCl.	Free acid calcd. as H_2SO_4.	Ammonia.	Albuminoid ammonia.	Nitric acid.	Oxygen required as permanganate.
Ireland, Valencia	48·67	2·73	6	None	·18	·03	·37	·05
Scotland, five coast country places, west ...	12·28	3·61	29	·14	·48	·11	·37	·02
,, eight coast country places, east ...	12·91	7·66	59	2·44	·99	·11	·47	·65
,, twelve inland country places ...	3·38	2·06	61	·31	·53	·04	·31	·26
England, twelve inland country places ...	3·99	5·52	138	None	1·07	·11	·75	·47
Scotland, six towns ...	5·86	16·50	282	3·16	3·82	·21	1·16	1·86
Germany, Darmstadt ...	·97	29·17	2998	1·74	—	—	—	—
England, London	1·25	20·49	1645	3·10	3·45	·21	·84	—
,, six towns ...	8·70	34·27	394	8·40	4·99	·21	·85	2·74
,, Manchester ...	5·83	44·82	768	10·17	5·96	·25	1·01	3·22
Scotland, Glasgow ...	8·97	70·19	782	15·13	9·10	·30	2·44	10·04

In these analyses it is to be noted that the chlorine is mainly due to the dried-up particles of sea-water cast into the air as spray. The amount is always greatest near the sea and smallest far inland; it is greatly influenced by the direction and force of the wind. Sulphuric acid is also partly attributable to the same cause, but if its ratio to the chlorine be more than 12 : 100 (the ratio in sea-water) combustion of coal or the decay of animal or vegetable matter is probably to be assigned as one of its sources.

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* Jour. Chem. Soc. 1872, 33.

Another extensive series of analyses of rain-water collected at Rothamsted was made by Frankland and published in 1881 and 1882* by Lawes, Gilbert, and Warington. From 69 samples collected in 1869-70 the following numbers were obtained. (Parts per million):—

	Nitrogen. As ammonia.	As nitric acid.	As org. matter.	Total solids.	Chlorine.	Hardness.
Mean ...	·37	·14	·19	33·1	3·1	4·7
Maximum	1·28	·44	·66	85·8	16·5	16·0
Minimum	·04	·01	·03	6·2	·13	0·0

In 1888-89 a series of monthly determinations of the amounts of ammonia and nitric acid in the rainfall at Rothamsted was made by Warington.† The results are given in the accompanying table:—

		Rainfall. Inches.	Per million of rain, N. as ammonia.	N. as nitrates.	Per acre (in lb.). N. as ammonia.	N. as nitrates.
1888.	May ...	1·28	·256	·109	·074	·031
	June ...	4·87	·500	·167	·551	·184
	July ...	3·86	·388	·104	·338	·091
	Aug. ...	3·38	·288	·090	·220	·069
	Sept. ...	1·03	1·025	·253	·238	·059
	Oct. ...	1·09	·525	·173	·129	·043
	Nov. ...	4·46	·313	·096	·315	·097
	Dec. ...	1·69	·500	·155	·191	·059
1889.	Jan. ...	1·29	.575	·190	·168	·055
	Feb. ...	1·95	·238	·095	·105	·042
	Mar. ...	1·89	·400	·136	·171	·058
	April ...	2·48	·575	·230	·323	·129
Whole year	...	29·27	·426	·139	2·823	·917

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* J.R.A.S. 1881 and 1882. † J.C.S. 1889, 537.

This gives a total of combined nitrogen in the rain of 3·74lb. per acre per annum.

The mean amount from seven Continental agricultural stations between 1864 and 1872 is 0·47 parts per million of nitrogen as nitric acid and 1·26pts. per million of ammonia in the rain, yielding a total fall of 10·18lb. of combined nitrogen per acre.

Results obtained in New Zealand and in Japan agree better with the Rothamsted results.

On the other hand, Müntz and Marcano* in 1883-1885, as the result of over 120 analyses of rain-water in Venezuela, found as a mean 2·23pts. of nitric acid per million (equal to 0·578 parts of nitrogen), the maximum amount being 16·25 (4·2 parts of nitrogen) and the minimum 0·2pts. (·05 nitrogen) per million. In the island of Réunion an average of 2·67pts. per million of nitric acid (equal to 0·69 parts of nitrogen) was found. As the rainfall, too, is much greater, it is obvious that the amount of nitric nitrogen conveyed to the soil by the rain is very much greater in the tropics than in England.

The same authors in 1890† found a mean of 1·55mgm. of ammonia (=1·28mgm. of nitrogen) per litre in rain-water collected in the tropics. Here, too, the amount is much greater than in England.

Ozone, the active form of oxygen, is present in air, but in very varying and always excessively small amount. The measurement of the absolute proportion of ozone in air is difficult, and the greater number of observations recorded merely give the relative amounts according to an arbitrary scale (Schönbein and Houzeau). Moreover it is very probable that many of the results obtained are really due, wholly or in part, to the presence of hydrogen peroxide.

Houzeau, who estimated the relative amount of ozone present in air by the colour imparted to strips of red litmus paper coated for half their length with 1% solution of potassium iodide and exposed for a given time, concluded that the amount of ozone in country air was, at the most, 1 in 450,000 by weight or 1 in 700,000 by volume. He observed that the amount was greatest in May and June and least in December and January, and that during rain and particularly during violent thunder-storms and gales the amount was often greatly increased. Over marshes or in towns no ozone can be detected.

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* Compt. Rend. 108, 1062; J.C.S. 1889, abst. 923.

† Compt. Rend. 114, 184.

According to Schöne[*] the indications usually ascribed to ozone are really due to hydrogen peroxide. In 1874 and 1875 he made many determinations (in Moscow) of the amount of hydrogen peroxide in rain and snow, also, by artificially producing hoar frost, in air. He found the maximum amount occurred in air at 4 p.m. and the minimum between midnight and 4 a.m., and that it was most abundant in July and least abundant in December and January.[†]

It seems established as a fact that country and sea air contains a powerful oxidising agent in small quantity, that this substance, whether it be ozone or hydrogen peroxide, is destroyed by contact with organic putrescible substances, and that the fact of its presence in any particular sample of air is practically an indication of the purity of that air. The popular belief in the health-giving character of "ozone-laden" air is thus seen to possess a real foundation in fact, but not in the way it is generally supposed. The ozone is not of itself important, so far as is known, except as proof of the purity of the air from all readily oxidisable ingredients, and probably from germs of micro-organisms. It has been shown that ozonised air quickly destroys germs in air.[‡]

According to Bach[§] hydrogen peroxide is present in the leaves of a large number of plants, being produced by the decomposition of carbon dioxide in presence of water by the chlorophyll of the plants. J. Peyrou[‖] found that ozone (or hydrogen peroxide) was evolved from growing plants. He found that more ozone was in nearly all cases to be detected in the air over a field with a growing crop than over a fallow field. He noticed that the amount of ozone was fairly constant during the day in August, but that from 6 to 9 p.m. no ozone could be found in the atmosphere.

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[*] Ber. 1880 [13], 1503.

[†] Abst. in Jour. C. Soc. 1878, 552.

[‡] Chappuis, J.C.S. 1881, abst. 632.

[§] J.C.S. 1895, abst. 26 and 239.

[‖] C. Rend. 1894, 1200; J.C.S. 1895, abst. ii., 240.

Determinations made by Thiérry on Mont Blanc showed* 3·5—3·9 milligrams of ozone in 100 cb. metres of air at Chamounix (1050 metres), while at the Grand Mulets (3020 metres) 9·4 milligrams per 100 cb. metres were present.

At Montsouris (Paris) the amount found was 1·9 to 4·0 milligrams per 100 cubic metres of air. It thus seems highly probable that the air from great altitudes contains more ozone or hydrogen peroxide than that near the surface of the earth.

A marked diminution in the average amount of ozone in the air at Montsouris, Paris, and Marseilles was noted during the outbreak of a cholera epidemic in France in 1884, the proportion of ozone at Paris sinking from 2·0, the average of the same period of the previous year, to ·27, while at Marseilles the diminution was from 2·17 to ·86. This may have been caused by the prevailing wind bringing air charged with sulphur dioxide from the cities over the observatories.†

In addition to the substances already mentioned, which may be regarded as essential constituents, the atmosphere near towns and in manufacturing districts contains other, accidental, constituents. Some of these are very prejudicial to the life of plants. Sulphur dioxide, which eventually becomes sulphuric acid, is the commonest of these harmful impurities. It is derived chiefly from the combustion of coal, though the decay of animal and vegetable matter yields small quantities of sulphuretted compounds.

The acid character of town rain is to be judged from the analyses on page 31. It is mainly on account of this acidity of the air and rain that there is difficulty and, in many cases, impossibility of growing plants in our large towns, young grasses being especially affected.

Bailey‡ in 1892 described the results obtained by the examination of a large number of specimens of air collected in Manchester, Liverpool, and London, with the especial object of determining the sulphur dioxide present. It was found that in clear, breezy weather less than 1mgm. of sulphurous acid per 100 cubic feet was present in the air of Manchester; but during fogs the amount sometimes rose to as high as 34 to 50 milligrams.

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* J. C. Soc. 1897, abst. ii., 253. † Jour. Soc. Chem. Ind. 1885, 462.

‡ British Association Report 1892, 679 and 781.

The chief causes which prevent or interfere with the growth of plants in towns are:—

1. Diminished sunlight, often less than 50% of the intensity of the light in the country.
2. The amount of sulphurous acid in the air. In heavy, calm weather the amount is often 10 to 20 times that present in windy, clear weather. During fogs the amount is even greater.
3. The acidity of the rain. In Manchester often as much as 70 parts of sulphuric acid per million were found. It was noticed that the rime deposited on the leaves of plants during frost sometimes contained as much as 400 parts sulphuric acid per million.

Organic matter of a readily putrescible nature is also present in air where respiration of men or animals or decay of organic matter (*e.g.*, in marshy and malarious districts) takes place. To this organic matter, perhaps, rather than to the increased carbon dioxide and diminished oxygen, the bad effects of breathing the atmosphere of close and crowded rooms are to be ascribed. This organic matter is probably suspended, but is very finely divided.

Solid Matter.—Air always contains large quantities of suspended solids, some of which consist of micro-organisms and their spores. The total number of micro-organisms in a given volume of air can be estimated by aspirating a known volume of air through a wide tube coated internally with sterilised nutrient gelatine. The tube is afterwards kept in an incubator for a few days and the number of colonies of micro-organisms can be counted. By this and other processes the air of various places has been examined bacteriologically.* The number present varies enormously and is less at greater elevations. Thus at Norwich 18 organisms in 10 litres of air were found near the ground, 9 at a height of 180ft., and 7 at 300ft. At S. Kensington it was found in 1886 that an average of 279 micro-organisms fell on each square foot of surface per minute, and that an average of 35 were present in 10 litres of air.

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* P. F. Frankland, Pr. Royal Society, 40, 509.

In air are to be found dust particles of every description, blown up from the surface of the ground and consisting of fragments of very diverse character.

In addition, air, even at considerable heights, contains solid particles of a more definite and uniform character—the minute particles left by the evaporation of the tiny droplets of the spray from the sea. Each drop of the spray loses its water by evaporation and leaves an excessively minute particle of dust, which remains suspended in the air until washed out by rain. These saline particles are naturally most abundant near the coast, as is evident from the analyses of rain-water; but at places far inland, chlorine is to be found in rain-water, and sometimes in considerable quantities.

Rain-water thus supplies a considerable quantity of solid matter from the sea to the soil. At Valencia (Ireland) Smith found about 49pts. of chlorine per million; this would correspond to about 1·5pts. of lime and 1·0pt. of potash per million, assuming that the chlorine was due entirely to the spray of sea-water. This would mean the deposition of the equivalent of about 5 ounces of lime and about 3½ ounces of potash per inch of rain on each acre of land. At inland places the quantities are, of course, much less, and the amount of saline matter conveyed to the soil by rain is usually so small as to be almost negligible.

CHAPTER III.

THE SOIL.

SOIL is the layer of more or less disintegrated rock which covers a large portion of the surface of the earth and which is fitted, under proper conditions of climate, to support the growth of plants.

In addition to the mineral ingredients, which usually constitute the largest portion, all soils contain certain quantities of organic matter resulting from the decay of previous vegetable growths. Soils also contain living organisms and varying quantities of water and gases. The depth of the layer of soil varies, but it is generally from 9 to 12 inches. It rests upon the *subsoil*, which differs from it in being less weathered, not so rich in organic matter, and often lighter in colour; the difference in the last respect being due partly to the subsoil being poorer in the dark brown organic matter—humus—and partly to the metals—iron, &c., being in a lower state of oxidation in the subsoil. Since soil consists largely of disintegrated rock, it is evident that a knowledge of the composition of the rock beneath and of its constituent minerals is of considerable help in judging of the probable composition and character of a soil. An acquaintance, therefore, with geology and mineralogy is useful to the scientific agriculturist. Any detailed account of rocks, their origin, and characteristics would be out of place here; but a few words may fitly be said about the chemical composition and characteristics of a few typical soil-yielding rocks.

If we accept the nebular theory of the earth's origin, it is evident that all rocks must have been formed out of the original intensely heated matter which ages ago represented the earth. The greater portion of the rocks at present forming the crust has probably been through a succession of changes, at one time forming hard igneous rock, then broken down by weathering into débris, which in course of time was again consolidated into rock, in some cases to be again denuded. The rocks now found are classified in various ways by geologists. One convenient method is based upon the process by which they were formed. We thus get three principal classes :—

1. *Igneous rocks*, subdivided into (i.) Plutonic.
    (ii.) Volcanic.
2. *Sedimentary rocks*, subdivided into (i.) Mechanically precipitated.
    (ii.) Chemically precipitated.
3. *Metamorphic rocks.*

These terms are almost self-explanatory. Class 1, generally hard and silicious, often crystalline, comprises those rocks which have been formed by solidification from a fused state; class 2, those formed from the fragments of previous rocks by deposition, generally under water; class 3, rocks (generally of class 2) which have been altered in character since their deposition by high temperature and pressure.

Another method of classification is based upon structure. Thus we have :—

A. Crystalline rocks, *e.g.*, granite.
B. Vitreous rocks, *e.g.*; obsidian.
C. Colloidal rocks, *e.g.*, silicious sinter, nodules.
D. Fragmentary rocks, *e.g.*, sandstones, shales.

Rocks of class A and B are generally igneous in origin (exception—certain limestones, rock salt, gypsum, &c., which may be classed as crystalline). Class C have probably been deposited from solution. Class D are sedimentary in origin.

Class 1 include the oldest rocks, from which probably the other rocks have been formed. Rocks of this class generally contain several minerals.

Minerals are characterised chemically by possessing a perfectly definite molecular structure and yet showing great variation in composition. This is due to the power which similar isomorphous elements exhibit of replacing each other in a compound without altering its crystalline form or general characteristics. Thus in felspar, $K_2O.Al_2O_3.6SiO_2$, as it is usually represented, the potash is almost always replaced to some extent by soda, and the mineral can be traced through all intermediate stages to albite, with the ideal composition $Na_2O.Al_2O_3.6SiO_2$. So, too, in calcite, which is theoretically $CaCO_3$, traces of magnesium are invariably present, and the replacement of Ca by Mg may go on until the composition of the substance would be more correctly represented by $MgCO_3$.

Minerals important in agriculture because of their abundance are:—

Quartz.—This is, practically, pure silica, SiO_2, and is extremely abundant. It occurs in granite and many other igneous rocks. It is practically insoluble in water and so is little affected by weather. Usually, however, the other constituents of the rocks in which it occurs (*e.g.*, the felspar in granite, the cementing material calcium carbonate, clay, or ferric oxide in sandstone, &c.) disintegrate by weathering, and the quartz fragments become detached and are thus removed. Quartz, though the most abundant constituent in most soils, is of practically no value as a plant food.

Felspar may be *orthoclase,* $K_2O.Al_2O_3.6SiO_2$
albite, $Na_2O.Al_2O_3.6SiO_2$
oligoclase, $2(Na_2:Ca)O.2Al_2O_3.6SiO_2$
or *labradorite,* $(Na_2:Ca)O.Al_2O_3.3SiO_2$.

—Orthoclase, the most important of these, is very abundant, forming an essential ingredient in granite, gneiss, syenite, and many other rocks. Though a hard substance, felspar is very easily decomposed by the influence of the weather. Water containing carbonic acid attacks it readily, removing the larger portion of the potash and a portion of the silica in a soluble form and leaving eventually a residue containing pure clay or kaolin, $Al_2O_3.2H_2O.2SiO_2$. Clay, however, is usually contaminated with partially decomposed felspar containing still a portion of its potash. Felspar furnishes a considerable proportion of the potash of a soil.

Mica, $3Al_2O_3.K_2O.4SiO_2$, always contains considerable quantities of ferric oxide, which partially replaces the alumina; magnesia, soda, and lime, also, are usually present. This mineral occurs in many rocks, notably in granite and gneiss.

It is disintegrated by atmospheric agencies, but not so easily as felspar. It furnishes plant food by virtue of the potash, lime, and iron which it contains.

Calcium carbonate.—This occurs in a great variety of different forms, constituting, when crystallised, the various modifications of *calcite* (rhombohedral) and *aragonite* (rhombic), and in the massive form—the rocks *chalk*, *limestone*, and *marble*. As already stated, these substances contain magnesium in smaller or larger quantities, also iron, and often manganese, the metals magnesium, iron, and manganese partially replacing calcium. Rocks containing calcium carbonate also invariably contain notable quantities of phosphates. Limestones thus furnish important constituents of plant food and are almost indispensable in many of the processes which go on in soils under the influence of bacteria (*v.* Chap. IV.).

Silicates of magnesia are also extremely abundant. Many different varieties exist, among the most common being *talc* and *steatite*, $6MgO.4SiO_2.H_2O$ (usually also contains ferrous oxide and alumina), *hornblende*, *asbestus*, and *augite* $(Mg:Ca:Fe:Mn)O.SiO_2$, *chlorite*, $4Mg(Fe'')O.2SiO_2.Al_2O_3.3H_2O$, and *olivine*, $2(Mg:Fe)O.SiO_2$. Many of these also contain silicate of alumina, and both ferrous and ferric silicates.

Clay, in its pure form, occurs as *kaolin*, $Al_2O_3.2SiO_2.2H_2O$. Common clay, however, always contains iron (replacing the aluminium) and generally some imperfectly decomposed felspar, so that it serves as a source of potash and iron to plants.

The oldest igneous rocks probably consisted mainly of silicates and silica; granite, syenite, basalt, diorite, trap, &c., are types of such old rocks. Under the denuding influences of the weather, portions of their silicates are decomposed and the whole rock disintegrates and is carried away by running water to the sea, the alkalis (potash and soda), the greater part of the lime, and portions of the magnesia and silica being in solution; much of the silica and the silicate of alumina in suspension. In the sea and rivers the suspended matter speedily settles to the bottom, the heaviest and coarsest portion, consisting of large fragments of quartz and some felspar, mica, &c., first, then the more finely divided quartz, &c., and lastly, after a long time and only in deep water, the very finely divided clay falls out. The dissolved matters, consisting of compounds of potash, soda, lime, and magnesia, remain in solution until removed by the agency of living organisms, *e.g.*, shell-fish, coral polyps, or sea plants.

In this way are formed accumulations in the bed of the ocean which, under pressure subsequently applied, will furnish grits, sandstones, shales, and limestones respectively, the latter being mainly composed of the débris of marine crustacea. The dissolved silica is also removed by diatoms, whose silicious skeletons sink to the bottom and remain admixed with the calcareous materials. Sedimentary rocks are thus divided into the three great classes :—

1. *Sandstones*, *grits*, and *conglomerates*, whose main ingredient is quartz, almost always mixed with some felspar and mica, and having their grains cemented together by either calcium carbonate (calcareous sandstone), clay (argillaceous sandstone), ferric oxide (ferruginous sandstone), or soluble silica (silicious sandstones).
2. *Shales* or *clays*.—These are mainly composed of kaolin, but also contain finely divided silica, particles of imperfectly decomposed felspar, and often considerable quantities of ferric oxide.
3. *Limestones*, including chalk and magnesian limestones. Here the chief ingredient is calcium carbonate, but magnesium, silica, iron, aluminium, phosphoric acid, and other substances are almost always present in varying proportions.

In addition to these are some few rocks formed in other ways. Thus by precipitation from solution, either by loss of carbonic acid, when calcareous deposits such as *tufa*, *travertine*, *sinter*, result; or by evaporation, by which *gypsum*, *rock salt*, the Stassfurth deposits, &c., were probably formed. Then, too, by the agency of animals, phosphatic deposits, *e.g.*, *guano*, *coprolites*, *bone-earth*, &c., have been produced, while the remains of plants have given rise to the important rocks *coal*, *lignite*, *peat*, &c.

Metamorphic rocks partake of the nature of both igneous and sedimentary, many having been formed from the latter by chemical and physical changes produced by great pressure or high temperature. As a rule they tend to show a crystalline character and are often hard and very similar to true igneous rocks. Sandstones become changed by metamorphism into *quartzites*. Shales become *slate* or even *gneiss*. Limestones are converted into *marble*.

The inorganic portion of a soil is really the insoluble portion of the débris resulting from the weathering of the rock on which it rests. It is, in fact, the disintegrated rock which has not yet been carried away to the final resting-place of all products of denudation—the ocean.

By the decay of igneous rocks there result, as has already been described, the materials which, when separated according to the order in which they settle out from suspension and solution in water, would form grits, sandstones, shales, and limestones. Soil formed by the decay of such a rock might be expected to have the composition of such a mixture, and to a great extent this is actually the case, except that the soluble products of denudation, viz., the carbonates of potash, soda, lime, and magnesia, have been to a great extent carried off in the drainage water.

By the decay of *sandstones* there results a soil composed very largely of grains of silica, but generally containing in addition whatever fragments of other minerals there might be in the rock, most commonly particles of felspar, mica, oxide of iron, and clay. Such soils are usually light and friable and poor in the main inorganic constituents of plant food, with the exception of potash, which is sometimes sufficiently abundant because of the felspar or other potash-containing minerals present.

Shales, consisting essentially of the very plastic hydrated silicate of alumina, when disintegrated tend to yield heavy clay soils, generally sufficiently well provided with potash, but often deficient in phosphates and lime.

Calcareous rocks, including chalk, limestone, and marble, are rapidly eroded by the combined action of water and carbon dioxide, their calcium carbonate being removed in solution, and the foreign bodies, *e.g.*, flint, sand, clay, oxide of iron, &c., left behind on the surface. It thus often happens that the surface soil on limestone is almost free from calcium carbonate and would be benefited by the application of lime. In the case of many limestone soils the actual inorganic matter in the soil probably does not exceed 1% of the amount of limestone which must have been denuded in order to leave it.

Transported soils.—Many soils are produced from the decay of rocks other than those upon which they rest. The rich alluvial soils of wide valleys contain inorganic materials which have been transported from a distance by the river and deposited there. The materials in many cases have been brought from various rock formations, and the resulting soil consequently possesses a greater fertility than would be shown by a soil formed exclusively of the débris of any one kind of rock.

Other means of effecting transportation are provided by glaciers. Large areas of land have, in many places, been covered with a thick deposit of débris brought from a distant source by moving ice. Such deposits are known as glacial drift and often consist of a finely divided clay matrix holding blocks of hard rock, which in some cases show the marks of ice scratches and have been brought from an immense distance.

Wind is sometimes a means of transporting matter from a distance and depositing it so as to form a soil. This occurs with sand near the sea coast or on the shores of large lakes, and also, over greater distances, with the ashes ejected from volcanoes.

The formation of soils is mainly brought about by the following agencies :—

1. **Water.**—This acts in various ways :—

(i.) *Mechanically.*—The flow of water over a rock subjects it to slight abrasion ; this is greatly increased by the pebbles, stony fragments, &c., which are urged by the current over its surface. In this way rapid streams and rivers carry down large quantities of materials from high ground and deposit them in the low-lying plains, giving rise to alluvial deposits. This action becomes most evident after heavy rains, when the water becomes muddy and discoloured.

(ii.) *By alternate frost and thaw.*—Ice, as is well known, occupies more space than the water from which it is formed. The increase in volume amounts to about 10%, and the force exerted by water in freezing is almost irresistible. Indeed, freezing cannot take place without this expansion, and if it be prevented the water remains liquid, though its temperature be reduced much below 0° C. It is found that if an additional atmosphere of pressure be exerted upon water its freezing point is lowered by ·0075° C. The bursting of water pipes in winter is a familiar consequence of this expansion in freezing.

In nature the disintegration of rock is greatly aided by this action of water. During the warm part of a winter's day the crannies and crevices of a rock become filled with water. As the temperature falls the water begins to freeze, at first on the outside, so that every crevice becomes stopped with a plug of ice, the still fluid water behind the plug continues to lose heat, and therefore tends to solidify. This it can only do if it can increase its bulk by about 10%. In order to do this it must either widen or lengthen the crevice which contains it. When the next thaw comes, the widened or deepened crevice again fills with water, and in the next frost repeats the action described. This process, going on at hundreds of places on the surface of a rock, soon breaks it up into smaller fragments, and these in turn are subjected to the same action. The process is necessarily confined to the outermost layer and is only of much importance when frost and thaw alternate rapidly. Long continued frost appears to protect rocks from weathering, the ice formed cementing the whole surface together.

(iii.) *As glaciers.*—Glaciers have played a very important part both in grinding and wearing down rocks into the finest powder and also in transporting the materials, in some cases for hundreds of miles. The water which issues from the snout of a glacier is always heavily laden with the finest mud, and huge heaps of débris, known as moraines, mark the successive positions of the termination of the glaciers. The fine portions of the glacial deposits possess a composition similar to that of the rock from which they were formed, comparatively little chemical change having taken place in their production.

(iv.) *Chemically.*—As already stated, many minerals, *e.g.*, felspar, exposed to the action of water, undergo chemical changes leading to their disintegration. In many cases soluble compounds are produced and carried away in solution by the water. This is pre-eminently the case with calcium carbonate, which, though almost insoluble in pure water, dissolves readily in water containing carbon dioxide, probably because of the formation of calcium bicarbonate, $Ca(HCO_3)_2$. Hence it is found that all river and spring waters contain dissolved mineral matter, and in many cases calcium carbonate is the largest constituent. The action of water on felspar has already been described.

In these and in other ways water, by its solvent properties, aids greatly in rock disintegration.

2. **Air.**—This also acts in several ways :—

(i.) *Mechanically.*—In mountainous districts high winds undoubtedly act destructively upon rocks both by the actual pressure exerted on projecting portions and also by hurling pebbles and smaller fragments of rock against them. The same action is sometimes seen in the production of fantastic forms in sandstone, produced by the erosion due to sand blown by the wind against the lower portion of a projecting rock, giving rise to an undercutting. This action, well shown at Brimham Rocks, in Yorkshire, is probably not a very important one.

(ii.) *Chemically.*—Many rocks contain the lower oxides of metals, especially of iron. On exposure to air such oxides combine with an additional quantity of oxygen, in so doing altering their volume and changing their colour. The change in volume, accompanied very often by falling to powder, aids in breaking up the rock. Air in the presence of water also oxidises metallic sulphides, *e.g.*, iron sulphide, and so produces disintegration in rocks containing such compounds. The carbon dioxide of the air, acting with water, is necessary for many of the chemical changes described as being due to water.

3. **Earth-worms** play an important part in the formation and modification of soil. Darwin* has shown that they bring portions of the subsoil to the surface, render the soil more porous and pulverulent, and aid greatly in the conversion of vegetable refuse, leaves, &c., into humus. This they do partly by drawing dead leaves, &c., into their holes, and partly by actually passing the vegetable matter and the soil containing it through their bodies. This matter is ejected and deposited on the surface of the ground at the rate of about 10 tons to the acre per annum, burying all small objects, like stones, fragments of bones, &c., to a depth which increases at an average rate of about $\frac{1}{10}$ of an inch per year. The number of earth-worms to the acre is estimated to average over 25,000, so that the part played by them must be most important.

4. **Vegetation.**—This acts in several ways:—
   (i.) *Mechanically.*—The roots of a plant penetrate the rocks or soil, rendering them porous, and so admitting air and water. Plants also tend to prevent the access of sunlight and air to the surface of rocks, and so favour their denudation by moisture.
   (ii.) *Chemically.*
      (a) *During life*, by the solvent action of the roots, which secrete an acid liquor capable of dissolving many constituents of rocks.
      (b) *After death*, by decaying and producing both acids of the type of humic acid and also carbon dioxide,

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* "Vegetable Mould and Earth-worms," 1881.

which is always found in large proportion in the air of a soil. These acids have powerful solvent properties.

5. **Bacteria.**—As will be discussed hereafter, ordinary vegetation requires the presence of nitrogenous organic matter, "humus," in the soil, and since the main source of this organic matter is the remains of previous plants, the question naturally suggests itself—What is the first source of organic matter in the mineral débris resulting from the disintegration of rocks? According to the observations of Müntz* the bare surfaces of the rocks even near the summits of mountains yield large numbers of nitrifying and other organisms which are able to withstand the lowest temperatures. Direct experiments showed that these organisms, with no other food than the mineral matter of the rocks and small quantities of ammonia and alcohol vapour in the moist atmosphere around, were able to live and produce nitrates, also to accumulate carbon. According to Winogradsky† these organisms by the energy liberated by the oxidation of ammonia to nitric acid are able to obtain carbon from mineral carbonates. It is evident, if these conclusions are correct, that bacteria must play an immensely important part in initiating the formation of the indispensable humus in soils. They are equally important in carrying on the functions of a fertile soil (*v.* Chap. IV.).

It is also to be noted that certain low forms of vegetation, *e.g.*, lichens and algæ, are apparently able to grow on a purely inorganic soil; they must therefore obtain the nitrogen they require from the air, possibly by the aid of micro-organisms associated with them. Such vegetable growth furnishes humus to a soil and renders it suitable for maintaining the life of higher plants.

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* Ann. Chim. Phys. [6], 11, 136; Jour. Chem. Soc. 1887, abst. 1135.
† Ann. Agron. 16, 273; Jour. Chem. Soc. 1890, abst. 1180.

The constituents of a soil are popularly divided into four groups, an arrangement which, though perhaps not scientific, is often convenient.

These proximate constituents are :—

(i.) Sand, consisting mainly of silica, but containing small fragments of felspar, mica, or even of limestone.

(ii.) Clay, mainly kaolin, but also containing finely divided felspar, &c.

(iii.) Finely divided limestone.

(iv.) Humus, the somewhat indefinite product resulting from the decay of organic matter in the soil.

Sand, from a chemical standpoint, is one of the least important constituents of a soil, furnishing as it does only very little of the food of plants. In fact, the essential constituents, the grains of quartz, are probably of no value whatever as plant food. The little plant food "sand" does provide is furnished by the fragments of felspar, mica, or calcium carbonate which may be present in it. From a practical point of view, however, sand is of the greatest value, because of the effect of its presence upon the physical texture of the soil. The importance of the physical condition of a soil is apt to be overlooked by a student of chemistry, but is often even greater than that of the chemical composition. Recently much attention has been paid to a study of the physical properties of soils, and valuable information is rapidly being accumulated, especially in America and Germany.*

The terms "light" and "heavy" as applied to soils possess a meaning well known to agriculturists, referring to the ease of working and really depending upon the tenacity or cohesion and not upon relative weight. As a matter of fact, the specific gravities of "light" and "heavy" soils are just the opposite to what the terms would seem to imply, the specific gravity of quartz being 2·62, that of clay 2·50, that of humus 1·3. However, the numbers quoted are the true specific gravities, *i.e.*, they represent the weights of a volume of solid quartz or solid clay compared to that of an equal volume of water. The

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* *v.* Warington, "The Physical Properties of Soils"; Wiley, "Agricultural Analysis," vol. I.; and King, "The Soil."

"apparent specific gravities" or the weight of a given volume of dry soil or powdered material compared with that of the same volume of water are much lower, since there are air spaces between the particles of the soil or powder

The apparent specific gravity of powdered quartz is found to be 1·449, of clay 1·011, and of humus 0·335.

The apparent specific gravity of a good arable soil will usually be about 1·2, its real specific gravity being about 2·5.

Sand is thus the heaviest of the main constituents and humus the lightest.

Sand confers friability, power of draining quickly, and good conductivity for heat upon a soil; it also has a low specific heat, consequently is soon rendered hot and cools quickly.

The specific heats of various soil constituents are given in the following table:—

	Equal weights.	Equal volumes.
Water	1·000	1·000
Humus	·477	·587
Clay	·233	·568
Calcium carbonate ...	·206	·561
Quartz	·189	·499

The average specific heat of a dry soil is ·20 to ·25 (equal weights).

The relative conductivities for heat are as follows:—

	Dry and light.	Wet.
Quartz powder ...	100	201·7
Peat ,, ...	90·7	94·3
Clay ,, ...	90·7	155·6
Chalk ,, ...	85·2	153·2

The conductivity, however, becomes greater with an increase in the coarseness and compactness of the material, as well as with an increasing amount of moisture, since the bad conductivity of all powders is due mainly to air spaces.

The amount of water held by the constituents varies greatly, thus 100pts. by weight

of sand were found to hold	25pts.	of water
of clay	70 ,,	,,
of fine calcium carbonate	85 ,,	,,
of humus	181 ,,	,,

It should be noted that the amount of water held by any powdered substance varies with the fineness of its particles; very fine sand, for example, will hold more than twice as much water as a coarser sand.

It is thus apparent that sand, which in most soils constitutes by far the largest ingredient, profoundly affects their relations to water and heat and thus their fertility.

Clay has characteristic physical properties which greatly affect any soil in which it forms a large constituent. As has been already stated, clay usually contains undecomposed or partially decomposed silicates, *e.g.*, felspar, containing potash, iron, and lime. It thus serves as a source of plant food. When carefully examined, it is found to consist of exceedingly fine particles, which in typical clay are kaolin ($Al_2O_3.2SiO_2.2H_2O$), but in common clays often partly quartz, felspar, or even (as in marls) calcium carbonate, cemented together with a colloidal form of kaolin, whose particles are so small as to escape detection even under the microscope. This colloidal or jelly-like form of clay only constitutes about one and a half per cent. of the whole, even in stiff clays, and it is probably more hydrated than the rest of the kaolin (Schloesing). It is upon the condition of this colloidal constituent that the peculiar properties of clay mainly depend. If it be in a fully swollen condition the clay is sticky and impervious, whereas if it be coagulated and shrunken the clay loses its stickiness and becomes quite workable.

If pure clay be mixed with a large quantity of distilled water a muddy liquid is obtained which shows practically no sign of depositing its suspended matter. By the addition of a small quantity of a mineral acid, of many salts, or, best of all, of lime-water, coagulation of the colloidal clay occurs with complete separation as a flocculent precipitate. Salts of calcium are nearly as good as lime-water in causing this coagulation, while alkaline solutions tend to favour the diffusion of the colloidal clay and will even destroy the flocculation produced by acids or salts.

It is this action of lime or salts upon colloidal clay which causes the improvement in the texture of clay soils which is brought about by liming, also the quick settling of the clay particles when a muddy river flows into the sea, with the consequent production of deltas and bars. The waters of rivers remain muddy for a longer time if deficient in lime compounds, while rivers containing very hard waters soon clarify. Frost also produces to some extent the shrinkage and coagulation of colloidal clay.

Limestone.—This term in connection with the constituents of a soil must be taken to mean the finely divided particles of calcium carbonate, &c., which are present, acting, perhaps, in some cases partly as a cementing material to the quartz grains. As already stated, it furnishes plant food by virtue of the calcium, magnesium, and phosphoric acid which are always present in it. Its action in the soil, however, is more important than as a mere source of plant food. It acts upon the colloidal clay in a manner already described as characteristic of lime and other salts and thus modifies the physical texture of the soil. Perhaps its most important function in a soil, however, is to act as a weak base, with which acid products, formed by decomposition of the organic matter in the soil, can readily unite and by which their harmful acidity is destroyed. If such basic material be absent, the soil becomes "sour," as it is called, and unfitted for the growth of most crops. This sourness is generally due to the production of free organic acids of the humic acid type and is possessed by many peaty soils where the amount of organic matter is excessive. The acidity is often apparent in such soils by the bleaching effect they have upon the sand and gravel upon which they rest. In many cases all the iron, &c., to which the gravels and sands owe their colour is found to be washed out by the acid drainage from the peaty soil.* Then still more important is the part played by calcium carbonate in the process of *nitrification* (*v.* Chap. IV.). Some basic material is essential for the continuance of this process, and the base is most generally found in the easily decomposable carbonate of lime or magnesia.

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* Another possible explanation of this bleaching action is that the organic matter draining from the peat reduces the ferric oxide to ferrous oxide, which is converted first into carbonate and then into the soluble bicarbonate by the carbon dioxide also abundant in the drainage water.

Carbonate of lime is also active in the changes which accompany the application of many manures to the soil, notably so in the case of sulphate of ammonia.

Humus, the organic matter of the soil, is of great importance both from its physical and chemical properties.

As has already been stated, it is a light, bulky substance, having a high specific heat, great capacity for holding water, and a dark colour. This last property is of considerable importance as affecting the absorption of the sun's heat; dark soils are found to become heated much more readily by the sun than light-coloured ones, while their radiating powers, by which they are cooled at night, are practically the same, the radiation being of obscure heat, while the absorption was of the intense radiant heat.

Schloesing[*] has shown that humus, or rather calcium humate, is a colloidal body possessing greater cementing power than clay in the proportion of about 11 to 1. It is thus highly important in sandy soils as a cementing material as well as on account of its power of retaining water. On the other hand, it has been shown that in clay humus materially lessened the plasticity and coherence.

The chemical nature of humus is still very imperfectly known. According to Mulder,[†] from 2·5 to 4·0 % of nitrogen is present. Many experimenters have obtained from the dark brown substance known as humus, several distinct bodies, amongst others *humic acid*, *humin*, *ulmic acid*, *ulmin*, *crenic acid*, and *apocrenic acid;* but little definite knowledge is possessed of the character and composition of these acids.

Humic acid was obtained by Detmer[‡] by treating peat with a solution of potassium carbonate and precipitating with hydrochloric acid. After repeated purifications an amorphous substance corresponding in composition to the formula $C_{20}H_{18}O_9$ was obtained; it still, however, contained ·179 % of nitrogen. It is described as being soluble in 8300pts. of cold or 625pts.

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[*] Compt. Rend. 74, 1408; J.C.S. 1872, 839.
[†] Annalen 36, 243.
[‡] Landw. Versuch. Station, XIV. 248; J.C.S. 1872, 521.

of boiling water, it reddens litmus, and expels carbon dioxide from carbonate, forming humates which are all insoluble with the exception of those of the alkalis.

The ammonium compound $C_{60}H_{48}(NH_4)_6O_{27}$ is very soluble in water. With calcium chloride a compound $C_{60}H_{46}Ca_8(NH_4)_2O_{27}$ is precipitated. Ulmic acid is stated by Detmer to be identical with humic acid. Crenic and apocrenic acids are produced by oxidation of humic acid. The former is said to be found in moist soils, the latter in dry, loose ones. Crenic acid is said to have the composition $C_{24}H_{24}O_{16}+3H_2O$, apocrenic acid $C_{24}H_{12}O_{12}+H_2O$.* The free acids are soluble in water.

The following gives some of the formulæ which have been proposed for the constituents of humus :—

	Thenard.	Detmer.	Mulder.	Stockbridge.
Humic acid	$C_{24}H_{10}O_{10}$	$C_{60}H_{54}O_{27}$	$C_{40}H_{24}O_{12}$	$C_{21}H_{24}O_{12}+3H_2O$.
Humin			$C_{40}H_{30}O_{15}$	$C_{21}H_{24}O_{12}+3H_2O$.
Ulmic acid		$C_{60}H_{54}O_{27}$	$C_{40}H_{28}O_{12}$	$C_{40}H_{24}O_{12}+H_2O$.
Ulmin			$C_{40}H_{32}O_{14}$	$C_{40}H_{23}O_{12}+H_2O$.
Crenic acid			$C_{24}H_{24}O_{16}+3H_2O$	$C_{12}H_{12}O_8$.
Apocrenic acid			$C_{24}H_{12}O_{12}+H_2O$	$C_{24}H_{24}O_{12}$.

The correctness of any of these formulæ is greatly to be doubted, as they leave out of account the nitrogen which is always found in the analyses and which Mulder assumed to be present as ammonia.

In 1889 a study of the black soils of Russia was published by Kostytcheff,† in which he found that the humus contained from 4·0 to 6·65 % of nitrogen, a quantity greatly in excess of that in the original vegetable matter from which it was produced (1·6 to 2 %). He found that when wet vegetable matter (hay) was allowed to decay under a bell jar, air being injected daily, the dry matter considerably diminished, but that no loss of nitrogen occurred, so that the percentage of nitrogen increased from 1·27 to 2·04. He concludes that the nitrogen in humus exists mainly as proteid bodies, very little being as amide; that both bacteria and moulds aid in the conversion of vegetable matter into humus; that if decay occurs beneath water the vegetable structure is retained and peat results, if in air all trace of structure is destroyed by the leaves being passed through the bodies of worms, caterpillars, &c. He states that fungi aid greatly in disseminating humus (say from a dead root) through the soil. In black earth the humic acid is almost exclusively in combination with lime.

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* Mulder, A. 36, 243.

† v. abst. in Jour. Chem. Soc. 1891, p. 611.

According to Eggertz* the organic substance obtained by extracting a soil with alkalis, filtering, and precipitating the filtrate with an acid, is soluble in water, alkalis, ammonium carbonate, oxalate, or phosphate, and in sodium or potassium carbonate, but insoluble in acids, ammonium chloride, sulphate, and nitrate, and in potassium sulphate and phosphate. The calcium compound is insoluble in water and alkalis. The potassium or sodium compounds are decomposed by most acids, but not by carbonic or boric acid. The substance is very complex and contains, apparently as essential constituents, small quantities of phosphorus, sulphur, and iron, in addition to carbon, hydrogen, oxygen, and nitrogen.

Thirteen analyses gave numbers between the following limits :—

Carbon	40·8 to 56·2 %
Hydrogen	4·3 — 6·6
Oxygen	25·1 — 38·0
Nitrogen	2·6 — 6·4
Silica	·37 — 10·5
Phosphorus	·15 — 7·6
Sulphur	·55 — 2·1
Alumina and ferric oxide	·38 — 3·9

The mineral matters associated with or included in the "humus" become soluble as the organic matter undergoes oxidation and yield an important quantity of plant food.

A number of analyses of humus were published by Snyder,† but they throw little light upon its constitution. The average composition of the ash of precipitated humus was as follows :—

Potash	7·5 %
Soda	8·1
Lime	·1
Magnesia	·3

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[*] Bied. Cent. 18, 75; J.S.C.I. 1889, 293.

[†] Journ. Amer. Chem. Soc. 1897, 738.

Alumina	3·5
Ferric oxide ...	3·1
Phosphorus pentoxide ...	12·4
Sulphur trioxide ...	1·0
Carbon dioxide ...	1·6
Insoluble	62·0

Analyses of four samples of humus obtained from soils gave

Carbon	44—50 %
Hydrogen	3— 6 %
Nitrogen	6·5—10 %
Oxygen	28—35 %
Ash	4—12 %

Humic acid and the soluble humates are colloidal bodies. According to Grandeau, humic acid and the humates combine with phosphoric acid, lime, potash, oxide of iron, or silicic acid to form double compounds, which, though soluble in ammonia, do not give the reactions characteristic of their constituents. When solutions of these double compounds are submitted to dialysis decomposition occurs and the ash ingredients pass through the membrane entirely free from the organic matter. This has, to some extent, been confirmed by Simon.* These absorptive properties of humus for substances in solution, as well as those of clay, are of great importance in agriculture and will be considered hereafter. Its alleged power of absorbing nitrogen from the air and converting it into ammonia, described by Simon and others, is denied by Prévost.† According to Loges‡ dilute hydrochloric acid extracts from a soil along with the humic acid a nitrogenous compound, whose composition could not be exactly ascertained; two samples from different soils contained 6·5 and 6·8 % nitrogen and 37·3 and 45·4 % carbon.

Classification of Soils.—Soils are usually divided by practical agriculturists into—

Sandy, containing less than 10 % clay and less than 3 % calcium carbonate.

Loam ,, from 40 % to 70 % clay and less than 3 % calcium carbonate.

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* Landw. Versuchs. Stat. 18, 452; J.C.S. 1876, 731.

† J.C.S. 1881, 371.

‡ Land. Versuch. Stat. 1885, 201.

Clay,	containing	from 70 % to 95 % clay and less than 3 % calcium carbonate.
Marl	,,	from 5 % to 20 % calcium carbonate, the rest mainly clay.
Calcareous	,,	more than 20 % calcium carbonate.
Peaty or humic		more than 20 % of humus.

The *colour of a soil* depends mainly upon the amount of humus and of oxide of iron which it contains and upon the quantity of moisture present. Organic matter tends to produce a black colour when moist and a grey when dry. Oxide of iron gives a well-known reddish tint, which, however, varies with its state of oxidation; if a soil is poor in organic matter and very porous, as is the case with sandy soils, although a large amount of iron may be present, the colour will not be a rich red but yellow. The rich red usually taken as a sign of fertility is produced when both oxide of iron and a considerable quantity of organic matter, and consequently moisture, are present. The oxide of iron in such cases probably acts as a carrier of oxygen from the air to the humus and so favours its decay, even in the presence of an amount of moisture which would interfere with direct oxidation by the air.

The *odour of soil.* When soil is moistened a peculiar odour is evolved. The cause of this was investigated by Berthelot and André in 1891.[*] They found it to be due to a volatile substance which they were not able to isolate, but obtained in aqueous solution by distillation with water. It possesses the peculiar odour of moistened soil, is not an acid nor alkali, does not reduce ammoniacal silver nitrate, and therefore is not an aldehyde; with potassium carbonate it gives a precipitate, and with potash and iodine it yields iodoform. Its amount is extremely small. According to Berthelot and André[†] clay soils kept in a moist state slowly lose nitrogen by the evolution of volatile nitrogen compounds; they also state that soils contain two classes of nitrogenous organic compounds, distinguished by their different rate of decomposition with cold potash solution.

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[*] Comp. Rend. 112, 598; J.C.S. 1891, abst. 858.
[†] C.R. 112, 195; J.C.S. 1891, 611.

CHAPTER IV.

THE REACTIONS OCCURRING IN SOILS.

THE chemical changes occurring in a soil are numerous and complex. To acquire a general knowledge of their nature and direction is difficult, especially as they are greatly influenced by circumstances, *e.g.*, temperature, strength of the solution with which the soil is moistened, free or difficult access of air, and a number of other constantly varying conditions. It is therefore only possible to indicate some of the actions which take place and to describe, to some extent, the effect thereon of variations in conditions.

The inorganic portion of the soil is subjected to the same actions of the air and water as gave rise to its formation from the original rock and which have been already considered. It is to be noted, however, that the changes probably proceed at an accelerated rate because of the larger quantity of carbon dioxide provided by the decomposing organic matter of the soil. Fragments of felspar, mica, and other minerals are thus exposed to the action of air and of water rich in carbonic acid. Their disintegration and the solution of the potash, lime, and magnesia which they contain thus proceed rapidly.

The reactions which occur are probably of a type which may be thus represented:—

$$\underset{\text{Orthoclase.}}{Al_2O_3.K_2O.6SiO_2} + CO_2 + 10H_2O$$

$$= \underset{\text{Kaolin.}}{Al_2O_3.2SiO_2.2H_2O} \quad + \quad \underset{\text{Potassium carbonate.}}{K_2CO_3} \quad + \quad \underset{\text{Silicic acid.}}{4H_4SiO_4}$$

Also—

$$Ca(HCO_3)_2 + Al_2O_3.K_2O.6SiO_2 + 9H_2O$$
$$= Al_2O_3.2SiO_2.2H_2O + CaCO_3 + K_2CO_3 + 4H_4SiO_4,$$

—the $CaCO_3$ acting as a carrier of CO_2; or if lime or magnesia be present; as, *e.g.*, in anorthite, proportionately more carbon dioxide is required:—

$$\underset{\text{Anorthite.}}{Al_2O_3.(CaO:MgO)2SiO_2} + 2CO_2 + 3H_2O$$

$$= \underset{\text{Bicarbonate of lime or magnesia.}}{(Ca:Mg)(HCO_3)_2} + \underset{\text{Kaolin.}}{Al_2O_3.2SiO_2.2H_2O}$$

The calcium carbonate present in the soil also becomes soluble—

$$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2$$

—and is either absorbed by the plant or carried away in the drainage water.

Exactly how the phosphoric acid exists in the rocks and minerals forming a soil it is difficult to determine. A portion probably occurs as calcium phosphate, $Ca_3P_2O_8$, and undergoes a change thus:—

$$Ca_3P_2O_8 + 2CO_2 + 2H_2O = \underset{\text{or } 2CaHPO_4.}{Ca_2H_2P_2O_8} + Ca(HCO_3)_2$$

The monohydrogen calcium phosphate, $CaHPO_4$, being slightly soluble in water, is available to plants.* It is possible, too, that the solution of calcium bicarbonate thus formed, together with that furnished by the calcium carbonate in the soil, may react upon such silicates as orthoclase and liberate their potash as carbonate, the lime uniting with the other constituents of the mineral:—

$$Al_2O_3.K_2O.6SiO_2 + Ca(HCO_3)_2 = Al_2O_3.CaO.6SiO_2 + 2KHCO_3.$$

The soluble potassium salt is then either absorbed by the roots of the crop growing on the soil or held in a weak state of combination by the hydrated silicates present.

The substances which become soluble owing to the action of water, carbon dioxide, and other reagents in a soil are not necessarily washed out of the soil by the drainage. The chlorides, sulphates, carbonates, and to a less extent, perhaps, the silicates, especially of lime and soda, are in great measure thus removed, the only action interfering with their complete removal being apparently the surface attraction exerted by the particles of the soil, an action similar to that exerted by charcoal towards salts in solution.

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* In the presence of ferric hydrate, often present in soils, the phosphoric acid of tricalcium phosphate is, by prolonged action of carbon dioxide and water, converted into ferric phosphate, the lime being removed as carbonate.—G. v. Georgievics, J.S.C.I., abst. 1892, 254.

With the potassium and ammonium salts and with phosphoric acid, however, the case is very different. In addition to the physical absorption or adhesion alluded to *(adsorption)*, there is a chemical retention exerted by certain constituents of soils for these substances. It can be shown by direct experiment that dilute solutions of potassium or ammonium salts or of phosphates, if filtered through a sufficiently thick layer of soil, are robbed of some of their constituents. In most cases the acids of the ammonium or potassium salts are found in the filtrate in combination with calcium.

This retentive power is apparently to be attributed mainly to the presence of hydrated silicates analogous in composition to the minerals known as *zeolites* (so called from their frothing, due to evolution of steam, when heated on platinum wire in the blow-pipe flame). It is, however, extremely unlikely that fragments of such minerals should exist in the soil, as they are, as a rule, easily decomposable and not very abundant in rocks. It seems more probable that the retentive substances are transition bodies produced in the weathering of such silicates as felspar, mica, &c., and consequently that they are not permanent ingredients in the soil and are present in an amorphous state.

The phenomenon of the retention of certain substances by soils was noticed by Bronner in 1836. It was investigated in 1850 by Way,* by Peters in 1860, by Knop in 1868, by Armsby in 1877,† and by van Bemmelen in 1878.‡

It is found that when salts are applied to the soil there is a replacement of one base by another (lime or soda from the hydrated double silicate), and that the absorbed oxide is only slightly soluble in water, more soluble in water containing carbon dioxide, and easily soluble in hydrochloric acid. The absorbed oxide can be re-exchanged by treating the soil with a solution of a salt of another metal. Alkaline hydroxides, carbonates, and phosphates are absorbed without any replacement. That the zeolitic silicates are the main agents in effecting this absorption is said to be proved by :—

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* J.R.A.S. 1850, 313.

† Amer. Jour. Sci. 14, 25.

‡ Landw. Versuch. Stat. 21, 135; J.C.S. 1878, abst. 598.

(1) Soils richest in silicates soluble in hydrochloric acid, have the greatest absorptive power.

(2) Soils treated with strong hydrochloric acid, which decomposes the basic zeolites, possess practically no absorptive power for salts, though they will still absorb, without exchange of metals, alkaline carbonates and hydrates.

(3) Powdered natural zeolites, *e.g.*, *chabazite*, a hydrated silicate of alumina, lime, and potash, have been shown to possess considerable power of exchanging their lime for other bases when treated with saline solutions.

The exact nature of the reactions by which the bases are retained has not been determined, especially as the composition of the zeolitic silicates in the soil is unknown. Assuming these substances to be analogous in composition to a mineral—*stilbite*, the change with potassium sulphate would be thus represented :—

$$Al_2O_3.CaO.6SiO_2.5H_2O + K_2SO_4 = Al_2O_3.K_2O.6SiO_2 + 5H_2O + CaSO_4.$$

—This reaction would in no case go to completion as represented, but equilibrium would be attained when the solution contained a certain ratio of calcium sulphate to potassium sulphate.*

Ferric hydrate and aluminium hydrate or hydrated basic carbonates of these metals are also present in some soils and have the power of retaining potash, lime, and ammonia, and to a still greater extent phosphoric acid (see foot-note on page 59). The bases, however, are absorbed without replacement and can be removed by prolonged washing with water. The absorption may possibly be due to the weak acidic properties possessed by ferric oxide and alumina, leading to the formation of salt-like compounds analogous to *spinel*, $MgO.Al_2O_3$.

It must be remembered that complete absorption never occurs, but that a small proportion of the substance always remains in the solution.

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* See Appendix to this Chapter for further explanation of such reactions.

The humus in a soil also possesses in a high degree the physical retentive power of all porous, bulky substances, and in addition it acts as an acid and forms insoluble humates with lime, magnesia, &c. It possesses great absorbent powers for ammonia. Whenever a soluble salt, of a strong acid particularly, is applied to a soil, interchange of base occurs to some extent; thus even sodium nitrate or chloride will cause the formation of potassium or calcium nitrate or chloride by interaction with the silicates of those metals present in the soil.

Phosphoric acid is mainly retained by the uppermost layers of the soil, especially if it be applied in the form of superphosphate; with dung some of the phosphoric acid is carried into the second or even the third 9 inches. With potash, although the uppermost 9 inches contains the largest quantity of the unused fertiliser, a considerable amount penetrates to and is retained by the second and third 9 inches.*

The distribution of dissolved matters in a soil is regulated partly by diffusion, *i.e.*, motion of the dissolved substances without that of the water as a whole and partly by motion of the liquid itself.

I.—*Diffusion* is the phenomenon by which a dissolved substance tends to pass from a greater to a less concentrated portion of the solvent. It is shown in different degrees by different substances. Colloidal bodies have the slowest rate of diffusion. The diffusibility of a salt depends partly on its acid and partly on its metal. The common acids and metals stand in the following order, starting with the most diffusible:—

Acids.	Metals.
Chloride	Potassium
Nitrate	Ammonium
Sulphate	Sodium
Carbonate	Calcium
	Magnesium.

II.—The liquid in the soil moves from various reasons:—

(a) The water, as a rule, exists as a liquid film upon the fine particles, and its position is partly determined by its surface tension or the force which tends to cause it

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[*] Dyer, Proc. Royal Soc., 1901, 11.

to take up a form with the minimum surface. Consequently if a portion of soil be only just moist the water films on its particles will be very thin and have relatively a large surface, while if another portion of the soil be very wet the water films in it will be thick and have relatively a small surface, and thus if the two portions of soil be placed in contact, the surface tension, which takes the form of a definite inward pressure per unit of surface, causes the water to move from the very wet to the less wet particles. This motion takes place in any direction, and may be either helped or hindered by gravitation. If, however, the interstices of a soil be completely filled with water, surface tension within the soil becomes zero and gravitation alone acts on the water. Thus when the surface soil becomes dried by evaporation, water from below is brought up by this passage from particle to particle, the impelling force being surface tension. Whitney has shown* that nearly all dissolved mineral substances increase the surface tension, while organic bodies and ammonia diminish it.

(b) *Gravitation.*—This of course always acts in the same direction, and, as has just been shown, is the only force acting on the water in a fully saturated soil. It greatly affects distribution of dissolved substances in soil, though its tendency to cause the liquid to sink in the soil is in many cases overcome by the surface tension phenomenon above described.

As a rule the motions of the water in a soil caused by the two agencies just described overpower the diffusive tendencies of the substances in solution. Thus in dry weather the water from the subsoil is brought up to the soil by the surface tension effect. Evaporation and consequent concentration of the solution takes place and the diffusive powers of the dissolved substances would tend to move them downwards to the weaker solution in the subsoil. This they undoubtedly do to some extent, but not as rapidly as the liquid moves upwards. The net result thus is that in dry weather the solution of plant food in the upper layers may be more concentrated than that in the subsoil. The roots of plants are probably, therefore, often bathed in a solution of plant food much richer in dissolved matters than is the drainage water from the same soil. For description of the methods by which plants obtain their food from the soil see Chap. IX.

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* Weather Bureau, U.S.A., Bulletin No. 4, 13.

Nitrification.—Important as the complex and little-known changes which affect the inorganic portions of soils undoubtedly are, quite as much interest and perhaps more fruitful labour have been directed to the study of the changes undergone by the carbonaceous and nitrogenous constituents. The organic matter in a soil is continually undergoing alteration, attended by the absorption of oxygen, and the consequent evolution of heat. This heat emission becomes greater when farm-yard manure is applied to land, and in some cases has been sufficient to raise the temperature of the soil 1° or 2° C. (Wagner). The air in the interstices of a soil is always poorer in oxygen and much richer in carbon dioxide than the air above it.

It is by changes of this kind that humus is produced from vegetable fibre (*v.* p. 54). Other organic acids are also formed by oxidation of vegetable matter, and if the soil be deficient in basic materials these acids may exert a baneful influence (as in so-called "sour" land).

Humus itself is not a permanent substance, but is continually being oxidised and broken down in a soil, a portion of its carbon being evolved as carbon dioxide, while its nitrogen passes eventually into the form of nitrates.

This latter change, the conversion of nitrogen existing as organic matter or ammonium compounds into nitric acid, is a most important one and has received an immense amount of attention of late years. It is known as *nitrification* and is effected, as indeed are probably all the changes of organic matter, through the action of micro-organisms.

The process of nitrification is an extremely important one, since in the case of the majority of plants it is only in the form of nitrates that nitrogen is assimilated. The organic nitrogenous matter existing in the soil is present in various forms, which appear to differ in their susceptibility of undergoing nitrification and also in their behaviour towards alkalis and acids.* All animal and vegetable refuse contains combined nitrogen, probably mainly in the form of proteid substances; as these undergo putrefaction in the soil and become converted into humus, carbon dioxide is evolved, and the nitrogen is probably converted into bodies of simpler constitution, amides,† ammonium carbonate, and in some cases, free nitrogen. As has been already shown, the form in which nitrogen occurs associated with humus is not known. It probably exists mainly as somewhat complex compounds, possibly of an amide character, or as amido-acids,‡ but of this, little knowledge has been acquired. These organic compounds are probably broken down in the soil, yielding first, ammonium compounds, *e.g.*:—

$$\underset{\text{Carbamide (urea).}}{CO\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right.} + \underset{\text{Water.}}{H_2O} = \underset{\text{Ammonia.}}{2NH_3} + \underset{\text{Carbon dioxide.}}{CO_2}$$

In this case the ammonia and carbon dioxide in the presence of water would yield ammonium carbonate $(NH_4)_2CO_3$. This change takes place very readily (as is shown by the smell of ammonium carbonate in stables, &c.) and is in all probability effected under the influence of a micro-organism. Indeed, according to experiments made by Müntz and Condon, and especially by Marchal,§ a large number of different bacteria and moulds are possessed of the power of converting the nitrogen of albumen into ammonia. Moulds probably do a large portion of the work in the case of manure heaps, humus, and very peaty soils; but in ordinary arable soils bacteria, of which *Bacillus mycoïdes* appears to be the most important, predominate. The bacterium just named is very widely distributed, constantly occurs in surface soils, in the air, and in natural waters. In decomposing albumen it produces ammonium carbonate with small quantities of formic, HCOOH, propionic, C_2H_5COOH, and butyric acids, C_3H_7COOH. No hydrogen or nitrogen is evolved in the free state. It requires the presence of oxygen, or if nitrates be present they are reduced to nitrites or even ammonia. Its action nearly ceases at 5° C., is greatest about 30°, and stops at 42°. It acts upon other nitrogenous organic compounds, *e.g.*, leucine, $CH_3.(CH_2)_3.CH(NH_2).COOH$, tyrosine, $HO.C_6H_4.CH_2.CH(NH_2).COOH$, creatine, $C_4H_7N_4O_3$, or asparagine, $C_4H_8N_2O_3$, but not upon urea, $CO(NH_2)_2$.

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* André, Compt. Rend. 1898, 414.

† *An amide* is a substance derived from an organic acid by the replacement of the OH group by NH_2. Thus from acetic acid $\left\{\begin{matrix}CH_3\\COOH\end{matrix}\right.$ is derived *acetamide* $\left\{\begin{matrix}CH_3\\CO.NH_2\end{matrix}\right.$; from carbonic acid $CO\left\{\begin{matrix}OH\\OH,\end{matrix}\right.$ *carbamide* (urea) $CO\left\{\begin{matrix}NH_2\\NH_2,\end{matrix}\right.$ &c., &c.

‡ Sestini J.C.S. 1899, abst. ii., 120. § Jour. Chem. Soc. 1894, abst. ii., 248.

The ammonium salts thus formed from the nitrogenous organic matter of the soil usually quickly oxidises again under the influence of a micro-organism, with the production of nitrous acid, or rather a nitrite, and finally, by additional oxidation, a nitrate is formed. The chemical reaction is simple:—

(i.) $(NH_4)_2CO_3+3O_2 = CO_2+2HNO_2+3H_2O$

(ii.) $2HNO_2+O_2 = 2HNO_3$

These changes, effected by the oxygen of the air, were shown in 1877 by Schloesing and Müntz* to be produced only under the influence of micro-organisms. Since then the subject has been carefully studied by Winogradski, Dehérain, Warington, Frankland, and many others.

The general conclusions arrived at may be stated as follows:—

1. The nitrogen of organic matter and humus is converted into nitrates by passing through the intermediate stages of ammonium compounds and nitrites, the successive steps being the work of different organisms. The production of ammonium compounds may be brought about by quite a number of bacteria and moulds, but the changes of nitrogen from the state of ammonia to a nitrite and from a nitrite to a nitrate are each apparently the work of only one particular organism called by Winogradski *Nitroso-monas* and *Nitroso-coccus*, capable only of effecting the oxidation of ammonia to a nitrite, and *Nitro-bacter*, capable only of converting nitrites into nitrates. The simpler terms *nitrous organism* (of which possibly two or more species exist) and *nitric organism*, used by Warington, are equally distinctive.

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[*] Compt. Rend. 84, 301; J.C.S. 1877, 215.

The change from organic nitrogen to ammoniacal nitrogen is always accompanied by oxidation of carbonaceous matter and the consequent production of carbon dioxide, the formation of which probably supplies the energy necessary for the reaction.

The other two stages of the reaction, ammoniacal nitrogen to nitrites and nitrites to nitrates, are themselves processes of oxidation and are consequently sources of energy. It is found that both the nitrous and the nitric organisms can effect their work in solutions free from organic matter and assimilate the carbon which they require for their growth from carbonates (Winogradski) or carbon dioxide* and without the aid of sunlight. Winogradski found that on the average 35 parts of nitrogen were oxidised for each part of carbon assimilated from carbonates. The necessary energy for this assimilation of carbon must be derived from the oxidation of the nitrogen. The oxidation of ammonia to a nitrite evolves about four times as much heat as the oxidation of the nitrite to a nitrate. Even the latter process evolves more heat than is necessary to account for the energy required in the experiments of Winogradski, 9 parts of nitrogen as nitrite oxidised to nitrate yielding sufficient energy to allow of 1 part of carbon being converted from carbon dioxide into cellulose.†

2. Nitrification can only occur under favourable conditions. The main essentials are:—
   - (a) *Suitable food.*—Certain minerals, particularly potash, lime, sulphates, and phosphates, must be present, and carbon dioxide is also essential. Organic matter is not necessary for either the nitrous or nitric organism. Ammonium compounds appear to be most easily nitrified, but the pure nitrous organism can apparently attack certain organic nitrogenous bodies, *e.g.*, asparagine, milk, casein, urea.
   - (b) *The presence of a basic material* in order to combine with the nitrous and nitric acid. The medium in

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* Godlewski, J.C.S. 1896, abst. ii., 668.

† Warington, J.C.S. Trans. 1891, p. 521.

which the process occurs may be slightly alkaline or neutral, but acidity or much alkalinity prevents nitrification. Calcium carbonate acts very efficiently as a basic material, the carbon dioxide being easily expelled or perhaps used for the assimilation of carbon by the organisms. Sodium bicarbonate $NaHCO_3$ is also suitable; but sodium carbonate Na_2CO_3 hinders or entirely prevents nitrification.

(c) *Suitable temperature.*—Nitrification probably ceases about the freezing point of water and it is stopped at a temperature of about 50° or 55° C. It is most active about 36° C.

(d) *Sufficient moisture.*—The action is suspended if a soil be air-dried.

(e) *Absence of strong light.*—Bright light, *e.g.*, sunlight, suspends the action of and eventually destroys the organisms.

(f) *Presence of sufficient oxygen.*—Since the process is one of oxidation it is obvious that free supplies of oxygen should be provided. Hence it cannot proceed in a waterlogged soil and is greatly increased by stirring the soil.*

(g) While the work of the nitrous organism proceeds obviously best in the presence of considerable amounts of ammonium salts, the nitric organism is rendered inactive by more than small amounts of such compounds and only produces nitrates when the ammonium compounds have, to a great extent, been destroyed by the nitrous organism.

(h) The action of the nitric organism is hindered by the presence of alkalis (sodium carbonate) or by calcium chloride, but is favoured by bicarbonates and sulphates.

(i) Nitrification can be stopped by the use of certain antiseptics, *e.g.*, chloroform or carbon disulphide vapour. It has even been suggested to employ the latter in autumn to lessen loss of nitrates by drainage from a soil.†

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* Dehérain. Compt. Rend. 116, 1091.
† Dehérain, Ann. Agron, 1895, 501; J.C.S. 1896, abst. ii., 329.

(k) Nitrification is stopped if the amount of ammonium carbonate present exceeds 400 parts of nitrogen per million, but 1000 parts of nitrogen as ammonium chloride do not prevent the action. Warington* found that the presence of gypsum effectively prevented the inhibitory effect of too large a quantity of ammonium carbonate by producing ammonium sulphate. The presence of gypsum would thus be advantageous in all cases where rapidly decomposing animal nitrogenous matter (*e.g.*, urea) has to be nitrified, for it would prevent the danger of the too rapid formation of ammonium carbonate, and consequent stoppage of nitrification (or even in some cases the destruction of the nitrifying organism).

(l) Potash compounds added to soils rich in humus have a favouring action upon nitrification, especially if the carbonate be employed, or if calcium carbonate be simultaneously applied.† Some of their results are given below :—

	Moor soil only.	Soil+4·5% K_2CO_3.	Soil+2·5% $CaCO_3$.	Soil+5% K_2SO_4.	Soil+2·5% $CaCO_3$ +5% K_2SO_4.
Amount of nitric nitrogen produced in 20 days, per million	25	438	30	18 to 25	189

Denitrification.—A chemical change involving the liberation of free nitrogen from nitrates takes place under certain circumstances in soils and in manure heaps. This process is effected by the agency of micro-organisms, several species of which appear to exist. The loss of nitrogen consequent upon this reaction is of serious importance and the subject has, of late, attracted considerable attention in France and Germany, as well as in England.

Bréal in 1892‡ showed that straw always contains micro-organisms which, in the absence of air, can produce free nitrogen, and to a small extent organic nitrogenous compounds, from nitrates. Wagner in 1895* by numerous experiments showed that the application of large quantities of organic manures, *e.g.*, farm-yard manure, cow-dung, &c., actually diminished the crop yielded by a soil, and to a great extent interfered with the increase otherwise produced by nitrate of soda. Maercker and other experimenters found similar results attended the use of farm-yard manure when used with nitrates; the manure not only did no good, but actually interfered with the action of the nitrate. The crop was both smaller and poorer in nitrogen. These results are apparently due to denitrification produced by the addition of the farm-yard manure, thus leading to the destruction of nitrates. By the German investigators the denitrifying organisms introduced by the manure are credited with the phenomenon, but it has been pointed out by Warington† and others that the farm-yard manure introduces into the soil another factor of importance, viz., a large increase in easily oxidisable organic matter, and this must greatly favour denitrification, both by lessening the gaseous oxygen in the soil and by actually tending to rob the nitrates of their oxygen. Nevertheless, it can hardly be denied that the micro-organisms are essential to the process, though it is not proved that there are not abundance of these actually present in soils, only waiting for favourable circumstances to perform their destructive work. Such favourable circumstances are a diminished supply of oxygen, even by consolidation of the soil,‡ and an increased quantity of oxidisable carbonaceous matter.

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* J.C.S. Trans. 1885, 758.

† Dumont and Crochotelle, Compt. Rend. 118. 604; Jour. Chem. Soc. 1894, abst. ii., 248.

‡ Compt. Rend. 114, 681; J.C.S. 1892, 1259.

In 1886 Gayon and Dupetit described two micro-organisms which they named *Bacterium denitrificans*, *a* and *b*, which in the absence of air effect the oxidation of organic carbonaceous matter by reducing any nitrates which may be present, nitrogen, or in some cases nitrous oxide, being evolved. In presence of air, nitrates are not reduced, but the oxidation is effected by the oxygen of the air.

Other varieties of this *Bacterium denitrificans* have been discovered, some obtained from soil, some found floating in the air.* The authors just alluded to ascribe denitrification to a reaction which they thus formulate:—

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* Journ. Agric. Prat. 1895, Aug. 26; also J.C.S. 1897, abst. ii., 428.

† J.R.A.S. 1898. ‡ Bréal, Ann. Agron. 1896, 32; J.C.S. 1896, abst. ii., 444.

$$\underset{\text{Sugar.}}{5C_6H_{12}O_6}+24KNO_3=24KHCO_3+6CO_2+18H_2O+12N_2.$$

This reaction is quite possible and would be attended with the evolution of heat.

Dehérain† found that the addition of starch to a soil resulted in the almost complete destruction of nitrates, but that when straw was added, even to the extent of 1% of the soil, only about $\frac{1}{3}$ of the nitric nitrogen was lost. He suggests that the injurious effects of large additions of farm-yard manure to a soil may be largely due to the nitrification being checked rather than to actual destruction of nitrates.

Soil Gases.—The interstices between the particles composing a soil are usually occupied by air, except when heavy rain or other cause fills them with water. This enclosed air must not be regarded as confined, but is constantly undergoing renewal by diffusion from the air above. Inasmuch as the processes going on in a soil are accompanied by, and indeed largely consist of, oxidation, it is obvious that the air within a soil will be poorer in oxygen than that of the atmosphere above. Schloesing‡ in 1890 published the results of a number of analyses of air sucked out from soil from various depths. This was always found to contain only the gases of the atmosphere, no measurable amount of marsh gas or other combustible gas being detected. The general results of these determinations were:—

1. The sum of the percentage amounts of carbon dioxide and oxygen is equal to 21.
2. The amount of carbon dioxide varies very much, from about 1% to as high as 8 or 10%, the oxygen from 10 to 20%.
3. In general the amount of carbon dioxide increases with the depth (up to 50 or 60cm.) from which the sample is collected. This is due not to diminished production near the surface, but to more rapid diffusion there.

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[*] Ampola & Ulpiani, Gazzetta, 1898, i. 410

[†] Ann. Agron. 1898, 130.

[‡] Compt. Rend. 109, 173.

4. Carbon dioxide is more abundant in summer and autumn than at other periods of the year.

In addition to the gases existing in the gaseous state in the interstices of the soil, considerable quantities are present in an absorbed condition. The various constituents of a soil possess very different powers of absorbing gases and vapours from the air. The following table* gives the maximum amount of water vapour, ammonia, and carbon dioxide which can be absorbed by 100 grammes of the various soil constituents at 0° and from an atmosphere containing the maximum amount of the aqueous vapour or from the pure gas, ammonia, or carbon dioxide:—

	Aqueous vapour from saturated air.		Ammonia.		Carbon dioxide.	
	Grams	C.C. (N.T.P.).	Grams.	C.C. (N.T.P.).	Grams	C.C. (N.T.P.).
Quartz ...	·159	199	·107	145	·023	12
Kaolin ...	2·558	3172	·721	947	·329	166
Humus ...	15·904	19722	18·452	22228	2·501	1263
Ferric hydrate ...	15·512	19236	4·004	5275	6·975	3526
Calcium carbonate	·224	278	·256	320	·028	14

If the soil be water-logged the decomposition of the organic matter proceeds in a different way, and marsh gas, CH_4, free nitrogen, and other gases are evolved. Such decomposition rarely occurs in a cultivated and properly drained soil.

The Water in a Soil.—The water in a soil is present to a great extent as a liquid film enveloping the particles composing the soil. This liquid film contains the soluble matter of the soil and its enclosed air. It consists, therefore, of a highly dilute solution of a large number of compounds. In a fertile soil it contains all the constituents of plant food (since they can only be assimilated by the plant in the soluble form†) and generally other substances non-essential to plants, *e.g.*, sodium and silicic acid.

The water retains the sodium chloride and sulphate originally present in the rain; but inasmuch as considerable evaporation always takes place, these substances become more concentrated.

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* Von Dobeneck, quoted by Wiley, Agric. Analysis (1894), Vol. I., 290.

† Or in some instances after being rendered soluble by the acid liquid secreted by the roots.

The composition of the water present in a soil can be deduced from analyses of drainage water, though doubtless the former is richer in dissolved substances.

Many analyses of drainage water have been made—at Rothamsted by Warington,* and at Grignon by Dehérain. At Rothamsted the average rainfall and drainage through 5 feet of bare soil were as follow:—

	Average of 16 years 1871—1886. Rainfall. Inches.	Drainage. Inches.
March	1·58	·66
April	2·32	·75
May	2·21	·54
June	2·56	·54
July	2·88	·61
August	2·50	·53
September ...	2·98	·88
October	3·39	1·71
November ...	3·13	2·09
December ...	2·55	1·94
January	2·69	2·10
February ...	2·25	1·60
Total, whole year ...	31·04	13·95
March to September...	17·03	4·51
October to February...	14·01	9·44

According to later results at Rothamsted the average for 20 years gives—rainfall, 30 inches; drainage from uncropped land, 14 inches. From a soil bearing a vigorous crop the amount of drainage is very much less (not much more than half), especially in summer, when drainage is often entirely suspended, except after very heavy rain. The composition of the drainage water will thus be altered, even if the crop does not actively exert any influence, for the dissolved matter should become more concentrated. But the plant exerts an influence in taking up and retaining much of the dissolved matter in the water, particularly the nitrates.

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* J.C.S. Trans. 1887, 500

The average amount of chlorine in rain-water at Rothamsted is about 2·0 parts per million. In drainage water from 60 inches of bare soil (equal, as is shown in the table just given, to not quite half the rainfall) the average amount is 3·9 parts per million and is very constant. Nitrogen as nitrates in drainage water from the same soil varied from about 10 in winter to about 14 parts per million in summer, the yearly average being 10·7, or a loss of about 40℔. per acre per annum. From unmanured wheat land the drainage water contained as the average for the whole year 6·0 parts per million of chlorine and 3·4 parts per million of nitrogen as nitrates, the latter varying from 4·3 in winter to 0·1 in summer.

In manured (farm-yard) wheat land the average numbers were 7·3 for chlorine and 5·8 for nitrogen.

From these numbers it appears that at Rothamsted the amount of chlorine in the drainage water is almost exactly equal to that supplied in the rain. From the results of a large number of analyses of drainage water and well waters, Warington concludes that 4·4 parts of nitrogen as nitrates per million is the average proportion in the drainage from cultivated land in the Rothamsted district.

Dehérain's experiments were commenced in 1892. His method of observation was to use 20 large water-tight cases 2 metres square and 1 metre deep, each holding 4 cubic metres, or about 5 tons of soil. These were filled with soil and subsoil. Access was provided to one side by means of a sunk path, so that the drainage water could be collected from the bottom of the cases. The results obtained during the first year were probably untrustworthy because of the increased nitrification due to the trituration and aeration of the soil in filling the cases. Reports as to the results are published annually in the "Annales Agronomiques." The Grignon soil is rich in organic matter and capable, if moist, of yielding large quantities of nitrates.

In the year March, 1896—March, 1897, the following results were obtained*:—

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* Jour. Chem. Soc. 1897, abst. ii., 591.

Case.	Crop in lb. per acre.	Drainage in inches.	Nitrogen as nitrates in ℔. per acre.
1	Fallow, not dug	11·11	186·7
2	Rye grass, 4754℔.	7·80	2·3
3	Oats, 1741℔., and straw, 4036℔. ...	7·29	7·4
4	,, 1634℔., ,, 3794lb. ...	7·92	12·7
5	,, 1634℔., ,, 3794℔. ...	8·04	23·4
6	Maize, green fodder, 62,500℔. ...	6·93	21·6
7	,, ,, 63,616℔. ...	6·66	14·7
8	,, ,, 66,964℔. ...	6·58	25·6
9	Wheat and vetches (wheat 1853℔., straw 3794℔., vetches 6696℔.) ...	6·62	12·8
10	Wheat only (wheat 1803℔., straw 3817℔.)	7·49	29·7
11	Wheat and vetches (wheat 1429℔., straw 3794℔., vetches 5803℔.) ...	6·86	7·1
12	Fallow, dug	11·54	196·4
13	,, not dug	11·15	157·9
14	,, dug and rolled	11·23	183·2
15	Potatoes, tubers, 24,553℔. ...	5·83	24·7
16	Vines, grapes, 16,786℔.	7·45	36·4
17	,, ,, 16,920℔.	7·41	75·0
18	Sugar beet, roots, 25,000℔. ...	7·17	2·4
19	,, ,, 29,241℔. ...	7·17	0·3
20	,, ,, 27,902℔. ...	7·64	0·3

The effect of vegetation in checking the loss of nitrates is clearly evident in these results. This it does in several ways: (i.) By actually absorbing the nitrates; (ii.) by lessening the amount of drainage by increasing the evaporation; and (iii.) in checking nitrification by rendering the soil too dry. This last effect is most marked when the period of most active growth corresponds with a dry portion of the year and is least evident when rain is abundant during that period. [Compare the results with maize (with late development)—the crop of which is estimated to contain 156℔. nitrogen per acre; this added to 20℔., the amount lost in drainage, gives 176℔. nitrogen per acre (almost equivalent to that produced on fallow)—with those with wheat (case 10), early growth during somewhat dry period; the crop is here estimated to contain 54·5℔. nitrogen per acre, which, added to the amount lost in drainage, 29·7℔., makes a total for amount of nitrogen converted into nitrates of only 84·2℔.; less than half that produced on the fallow cases.]

With reference to the loss of other constituents in drainage waters, Stoklasa* has determined the amount of calcium carbonate in drainage waters from soils derived from primitive rocks, from chalk, and from peaty soils. He estimates the yearly loss of calcium carbonate in soils from primitive rocks at over 560 kilos per hectare (500℔. per acre)† and at about 3000 kilos per hectare (2700℔. per acre) in soils from chalk. Its amount is increased by the application of ammonium compounds owing to the acid of these salts being converted into calcium salts by interaction with calcium carbonate, and also to the formation of the very soluble calcium nitrate from nitrification. He also gives the amounts of phosphoric acid found in the drainage water from (1) loam from granite and gneiss formations, (2) clay from the Permian, (3) marl, (4) humic soil. The results were as follows:—

	Loamy soil.	Clay soil.	Marl.	Humic soil.
Total P_2O_5 in soils ...	0·024	0·087	0·125	0·008%
P_2O_5 in drainage, per million	0·620	0·420	0·700	1·010
Estimated loss, ℔. per acre	12·00	8·13	13·60	19·60

This shows the enormous loss of phosphoric acid from humic soils, although they contain only very small quantities. This great loss is doubtless due to the solvent action of the large quantities of carbon dioxide contained in the drainage of such soils.

Few determinations of the amount of potash in drainage waters have been published.

Its amount is probably always very small and the loss of potash from this cause is seldom a matter of much importance. Any potash which becomes soluble, or is applied in a soluble form as manure, appears to be to a great extent held firmly in the upper layers of the soil.‡

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[*] Landwirth. Versuchs. Stat. 1894, 45, 161.

[†] Lawes, Gilbert, and Warington (J. Roy. Agric. Soc. 1882, 1) estimate the loss at about half this at Rothamsted, on unmanured land.

[‡] H. Liebig, J.C.S. 1872, 318.

On the other hand, American investigators found as much as from 0·43 to 44·0 parts of potash (K_2O) in a million of drainage water.[*]

Way found from 0·3 to 3·1 parts K_2O and up to 1·7 parts P_2O_5 per million of drainage water.[†]

Schloesing[‡] states that the amount of phosphoric acid in the water impregnating soils is usually about 1 mgm. per litre, but sometimes is as much as 2 or 3 mgms.

The composition of drainage water naturally varies with many circumstances, *e.g.*, rainfall, &c. Complete analyses have not recently been published. The average of analyses by Way (1856), Kröcker (1853), and Zöller (1857) gave the following:—

	Parts per million.
Potash, K_2O	2 to 60
Phosphoric acid, P_2O_5 ...	traces to 2
Lime, CaO	68 to 180
Soda, Na_2O	5 to 46
Silica, SiO_2	5 to 25
Sulphuric acid, SO_3 ...	18 to 130
Organic matter	16 to 180
Nitric acid, N_2O_5 ...	2 to 210
Ferric oxide and alumina...	0·7 to 7
Chlorine	1 to 57
Total solids (average) ...	365

Biology of the Soil.—Micro-organisms of various kinds have been found in air, water, soil, and almost all natural media. The soil, being the scene of such numerous processes of decay, oxidation, and chemical change, is found to be teeming with myriads of minute forms of life,[§] each engaged in carrying on the chemical changes essential to its growth, whenever the conditions are favourable. For specific information with reference to the history of micro-organisms and details as to the methods of investigating their nature and functions the student is referred to a manual of bacteriology, a subject which now has an extensive literature.

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[*] Massachusetts State Station Report 1883, p. 27.

[†] J.R.A.S. 1856, 133.

[‡] Compt. Rend. 127, 236; J.C.S. 1899 abst. ii., 119.

[§] Various estimates of the number of micro-organisms present in 1 gramme of soil (obviously the number will greatly vary) have been made, some authorities estimating them at from 750 000 to 1,000,000, while in a black peaty soil from Russia 60,000,000 were thought to be present.

The micro-organisms in a soil include moulds, yeasts, and bacteria, and in addition there are minute plants (*e.g.*, algæ), which grow, probably, only on the surface. These latter appear to be able to assimilate carbon and nitrogen from the air and build up organic compounds from inorganic materials (see p. 48, Chap. III.).

The fungi and yeasts act upon certain kinds of organic matter in the soil, the former using this material to build up its own structure and and then, by its decay, leaving again a residue which in many cases appears to be more susceptible to nitrification than the original. It is to such an action of a fungus, spreading outwards from a starting point, that the existence of those richer coloured and more luxuriant circles of grass in pasture fields known as "fairy rings" is due.*

The vital processes, too, of many of the moulds appear to be connected with important changes in nitrogenous organic matter (*e.g.*, the formation of ammonium carbonate from proteids).

But most interesting, perhaps, are the minutest forms of life known as bacteria. These bodies are of various external forms and are often classified into some four or five groups according to their characteristic appearance. Thus there are *bacilli* or rod-like organisms, *spirilla* or corkscrew-like, *micrococci* or spherical. Their size is very minute, being about $\frac{1}{1000}$ of a mm. in diameter and rarely exceeding $\frac{4}{1000}$ of a mm. in length. Bacteria multiply by simple fission, but many forms have the power, at intervals, of reproducing themselves in another manner, *viz.*, by spore formation. Spores are resting states of existence and can resist treatment which would, at once, kill the active form of the bacterium. For example, they may be dried and some even heated to 100° C. without destroying their power of germinating under favourable conditions.

Ordinary soils contain large numbers of different bacteria, some fulfilling useful functions in agriculture, some being destructive to plant food, and some highly injurious to animal life if they once gain admission to the proper portion of their victims (*e.g.*, the bacterium of tetanus or lock-jaw). Of the work of the nitrifying and denitrifying organisms a brief description has already been given; it remains here only to say a word or two about their appearance.

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* Lawes, Gilbert, and Warington, J.C.S. 1883, Trans. 208.

Of organisms possessing the power of converting organic nitrogenous substances into ammonium compounds a considerable number are known, as has already been stated, some being moulds (active especially where the quantity of organic matter is large), while others are bacilli, *e.g.*, *B. mycoïdes* (p. 65) and *B. fluorescens*, and micrococci, *e.g.*, *Micrococcus ureæ*.

Of organisms capable of effecting the oxidation of ammonia to nitrous acid there appears to be possibly more than one, but according to Winogradski only one is usually present in any particular soil.

The pure nitrous organism is described by Warington* as consisting of two forms of micrococcus. One form is nearly spherical in shape and varies in diameter from the very minute up to 1 micromillimetre (·001mm.). The other is oval shaped and larger, its greatest length being more than ·001mm.

The nitric organism isolated by Winogradski in 1890 is of very minute size, consisting of rods not more than ·0005mm. in length and from ·00017 to ·00025mm. in thickness.

The conditions favourable for the growth and development of these organisms have already been described. With reference to their distribution Warington found that nitrifying organisms did not exist at greater depths than 18 inches and were most abundant within a short distance from the surface. In later experiments he found that a few nitrifying organisms were present even at a depth of several feet. Winogradski† in 1893 obtained from soil a large bacillus which, when cultivated in a solution containing suitable mineral ingredients and pure dextrose and supplied with air purified by means of potash and sulphuric acid, caused the destruction of the dextrose ($C_6H_{10}O_5$), the formation of butyric acid (C_3H_7COOH), the evolution of carbon dioxide and free hydrogen, and the

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* J.S.S. 1891, Trans. 484.

† Compt. Rend. 116, 1385; J.C.S. 1893, abst. ii., 482.

formation of nitric acid. The nitrogen must have been obtained from the air. Subsequent experiments of Winogradski showed that the bacillus was anaerobic and if air were present could only assimilate free nitrogen by the aid of other micro-organisms which may have acted by removing the dissolved oxygen from the solution. The amount of nitrogen assimilated seems to bear some relation to the sugar consumed, but the action is greatly affected by the presence of combined nitrogen.

Cultures of an organism (known as *Bacillus ellenbachensis*), said to have similar properties, were made in Germany and sold under the name of "*aliniit.*" They have not been very successful in practice.

Another class of micro-organisms is of great importance in agriculture, viz., those which flourish in the nodular swellings on the roots of certain leguminous plants.

The great question as to the possibility or otherwise of utilising the free nitrogen of the air has excited much attention and an enormous amount of research has been devoted to its solution. That leguminous crops apparently increased rather than diminished the amount of nitrogen in the upper part of the soil, although they contained large quantities themselves, had been observed and use had been made of the fact in agriculture. No satisfactory explanation as to how this was effected was forthcoming until, in 1886, Hellriegel published an account of the bacteria which he found in the root nodules possessed by clover and other leguminous plants. In later papers, in conjunction with Wilfarth,* he clearly showed that, living in these nodules were bacteria *(Bacillus radicocola)*, which have the power of bringing about the assimilation by the parent plant of the free nitrogen of the air. From other investigations by the same chemists, and also by Nobbe and Hiltner, Schloesing and Laurent, and others, it has been proved that the various leguminosæ have different bacteria, and that assimilation of free nitrogen by a plant depends upon the presence in the soil of the particular micro-organism capable of growing in *symbiosis*† with it. The importance of this discovery attracted considerable attention, and pure cultures of the nodule bacteria were put on the market for application to soils which might be deficient in them. These preparations were known as *nitragin* and were not so successful in actual practice as had been hoped. They are, I believe, no longer commercially obtainable.

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* See abstracts in J.C.S. 1888, 742; 1889, 640.

† By this term is meant the living together of two organisms for their mutual welfare, as distinguished from *parasitism*, in which one organism preys upon another to its own advantage, but to the injury of the host.

Nevertheless, Hellriegel's discovery is very important and affords a satisfactory explanation of many hitherto puzzling facts in reference to the nitrogen question. Some investigators have obtained results which show that plants other than the leguminous ones assimilate free nitrogen, but to a much less extent.* With the exception of lupins, the author just quoted found that all the plants he tried were developed best when combined nitrogen was also supplied. In many cases the amount of free nitrogen assimilated was increased if combined nitrogen was also supplied.

Other experimenters, *e.g.*, Lotsy,† do not confirm the fixation of free nitrogen except in the case of leguminous crops.

According to later investigations the bacteria in the nodules of leguminous plants secrete an enzyme (*i.e.*, a so-called unorganised or soluble ferment) and the assimilation of the atmospheric nitrogen really occurs in the leaves of the plant under the influence of the enzyme.‡ That the fixation takes place in the leaves is denied by Nobbe and Hiltner,§ who found that if the nodules on the roots were kept under water, fixation of nitrogen ceased.

A summary of the natural sources of the nitrogenous food of plants may usefully be given here:—

(1) The ammonium compounds and nitric acid brought down in the rain (see Chap. III.).

(2) Gaseous ammonia absorbed from the atmosphere by the soil constituents. This is probably a comparatively unimportant source.

(3) Compounds of nitrogen (chiefly nitric acid, probably) formed by micro-organisms existing in the soil itself, air furnishing the necessary nitrogen and oxygen.

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* Frank, J.C.S. 1892, abst. 370.

† U S. Dept. of Agric., Bulletin 18, 1894.

‡ Stoklasa, Jour. Chem. Soc. 1900, abst. ii., 610.

§ Jour. Chem. Soc. 1900, abst ii., 234.

(4) Similar compounds produced by the micro-organisms (or by the enzymes resulting from them) frequenting the tubercles or nodules on the rootlets of leguminous plants.

(5) The products of the nitrification of organic compounds already present in the soil. This is also the work of micro-organisms.

(6) The small quantity of nitrogenous matter (in solution or suspension) brought in occasionally by flood water, and its subsequent nitrification, if necessary.

APPENDIX TO CHAPTER IV.

The chemical changes occurring in a soil take place between substances in highly dilute solution, and it is probable that considerable help might be afforded by the application of Arrhenius's electrolytic dissociation theory of solution to such problems.

It would be out of place to attempt complete exposition of this theory here, but it may perhaps be advisable to very briefly mention the chief conceptions contained in it.

When a compound capable of undergoing electrolysis in aqueous solution is dissolved in water, the mere act of solution is accompanied by its partial or complete dissociation into *ions*, as the metal and acid radical are called. Thus in a solution of common salt there are a number of molecules of NaCl, but if the solution be dilute the greater portion of the salt exists as free ions of sodium and chlorine, the ions consisting of atoms (in this case) each carrying a charge of electricity, positive in the case of the metal, negative in the case of the halogen. The degree of dissociation, *i.e.*, the proportion of the total quantity of salt which thus undergoes "ionisation," increases with the dilution.

The chemical changes which may ensue when two solutions are mixed are dependent upon the action of the ions upon each other. Thus, if to a dilute solution of NaCl a solution of silver nitrate be added we get a precipitate of silver chloride, because this substance, being insoluble in water, cannot undergo ionisation. The action which occurs is to be regarded thus: Both solutions contain chiefly ions, the one $\overset{+}{\mathrm{Na}}$ and $\overset{-}{\mathrm{Cl}}$, the other $\overset{+}{\mathrm{Ag}}$ and $\overset{-}{\mathrm{NO_3}}$. On mixing the solution a precipitate of insoluble AgCl separates owing to the union of the Ag and Cl ions, and the solution now contains not $NaNO_3$, as is usually taught, but really ions $\overset{+}{\mathrm{Na}}$ and $\overset{-}{\mathrm{NO_3}}$. On evaporation these ions unite and form $NaNO_3$, which may be obtained in crystals. All the changes which take place when aqueous solutions of salts are mixed are to be thus represented. The most difficult conception in connection with the theory is that the ions have not the usual properties of the free substances themselves, which in many cases could not exist in contact with water, but, because of their electrical charges, are utterly different. When the electrical charge is removed, as by electrolysis, the ions disappear and the material of which they are composed takes its usual properties.

Thus, to consider common salt solution, the Na ions possess none of the properties of sodium nor the Cl ions any of those of chlorine; but when a current of electricity is passed the Na ions are freed from their charge and metallic sodium is set free at one pole (cathode), and, being in contact with water, at once reacts, giving free hydrogen and caustic soda, while at the other pole (anode) the Cl ions lose their charge of negative electricity and are evolved as chlorine gas.

When a salt is dissolved in water, it may partially dissolve as such, that is, some molecules of the original salt dissolve; but decomposition into ions at once commences and goes on until there is a certain fixed ratio (for the particular salt and dilution) between the undecomposed salt and the products of the ions present. Take common salt, for example. The equilibrium will be reached when—

$$\begin{aligned} &k\ (\text{number of mols. of undecomposed NaCl}) \\ &= (\text{number of Na ions} \times \text{number of Cl ions}) \end{aligned}$$

(k being a constant which varies with the dilution and temperature, the numbers being those present in unit volume of the solution).

If another salt having ions of a similar kind be dissolved in the same solution, the equilibrium previously existent is disturbed. Suppose, for example, sodium sulphate were added to the common salt solution. The ions of the new salt are $\overset{+}{\mathrm{Na}}$, $\overset{+}{\mathrm{Na}}$, and $\overset{--}{\mathrm{SO_4}}$, and the conditions of equilibrium are determined by the equation—

$$k\,(\mathrm{Na_2SO_4}) = \overset{+}{\mathrm{Na}} \times \overset{+}{\mathrm{Na}} \times \overset{--}{\mathrm{SO_4}}$$

as before, k, of course, having another value; but in the mixture the Na ions are partly furnished by the common salt, partly by the sodium sulphate. The consequence is that inasmuch as the degree of dissociation of each salt depends partly upon the number of Na ions, less dissociation is suffered by each salt than would be the case if the other were absent.

It is found that nearly all salts suffer a large amount of dissociation in dilute solution, but that this is only the case with strong acids and strong bases. Weak acids and bases undergo little or no ionisation, and it is upon this fact that the weakness of the acid depends, the activity of an acid being really measured by the proportion of ionised hydrogen in its solution.

It is thus evident that when two neutral salts are mixed in dilute solution, if no insoluble or volatile product is formed by interaction of their ions, no chemical action really takes place. Thus, if sodium chloride and potassium nitrate be mixed together no evidence of chemical action is presented; indeed, none occurs, and in the mixed solution the ions $\overset{+}{\mathrm{K}}$, $\overset{+}{\mathrm{Na}}$, $\overset{-}{\mathrm{Cl}}$, and $\overset{-}{\mathrm{NO_3}}$ remain side by side.

If, however, two of the ions can unite and form a non-ionisable substance, then a decided interaction, accompanied usually by a thermal disturbance, occurs. Such a non-ionisable substance may be an insoluble body or it may be a soluble substance, *e.g.*, water, which is practically non-dissociated.

For example— $\overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{Cl}} + \overset{+}{\mathrm{Ag}} + \overset{-}{\mathrm{NO_3}} = \overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{NO_3}} + \underset{\text{Silver chloride.}}{\mathrm{AgCl}}$

Or again—
$$\underbrace{\overset{+}{\mathrm{H}}+\overset{-}{\mathrm{Cl}}}_{\text{Ions of hydrochloric acid.}} + \underbrace{\overset{+}{\mathrm{Na}}+\overset{-}{\mathrm{OH}}}_{\text{Ions of caustic soda.}} = \underbrace{\overset{+}{\mathrm{Na}}+\overset{-}{\mathrm{Cl}}}_{\text{Ions still in solution.}} + \underset{\substack{\text{Water.}\\ \text{Non-ionised.}}}{\mathrm{H_2O}}$$

Or—
$$\underbrace{\overset{+}{\mathrm{Na}}+\overset{-}{\mathrm{C_2H_3O_2}}}_{\text{Ions of sodium acetate.}} + \underbrace{\overset{+}{\mathrm{H}}+\overset{-}{\mathrm{NO_3}}}_{\text{Ions of nitric acid.}} = \underbrace{\overset{+}{\mathrm{Na}}+\overset{-}{\mathrm{NO_3}}}_{\text{Ions still free in solution.}} + \underset{\substack{\text{Acetic acid.}\\ \text{Very little ionised.}}}{\mathrm{HC_2H_3O_2}}$$

In the last case in the solution there would be a very few ions $\overset{+}{\mathrm{H}}$ and $\overset{-}{\mathrm{C_2H_3O_2}}$, as acetic acid is slightly dissociated. Indeed, in every case very small quantities of the ions of the assumed non-ionisable substance remain in solution, as probably no substance is absolutely non-ionisable, just as probably no substance is absolutely insoluble in water.

When a chemical reaction takes place simply between ions it is completed in an exceedingly short time, but if other changes occur, very often they do so slowly and the reaction extends over a considerable period.

Mass Action.—When two substances are brought into contact by one or both being in solution a reaction often occurs and goes on until equilibrium is attained.

This equilibrium is generally reached before the whole of a reaction as represented by an equation is completed. What actually occurs will perhaps be best understood by taking an example. If barium sulphate (insoluble) be treated with a solution of potassium carbonate a reaction begins, resulting in the formation of barium carbonate (also insoluble) and potassium sulphate, in accordance with the equation—

$$\mathrm{K_2CO_3+BaSO_4=BaCO_3+K_2SO_4}.$$

But this reaction never goes on to completion as is represented by the equation. When equilibrium is attained the solution is found to contain both potassium sulphate and carbonate and the precipitate both barium carbonate and sulphate. Moreover, it is found that if barium carbonate be treated with potassium sulphate solution a similar state of equilibrium is attained and the ratio between the number of equivalents of potassium sulphate and potassium carbonate present in the solution would be the same in each case (the ratio actually found is about 1:4). The reactions really take place in both directions at the same time, and equilibrium is attained when the velocities of the two opposing reactions are equal. The reaction may therefore be better represented thus :—

$$K_2CO_3+BaSO_4 \rightleftarrows K_2SO_4+BaCO_3.$$

As has been shown by Guldberg and Waage in 1867, the intensity with which two substances tend to react depends upon—

(1) The product of their *active masses*, *i.e.*, the number of equivalents of each of the substances present in the unit volume.

(2) Another factor, depending upon the nature of the two substances, the temperature, and other physical conditions of the reaction.

Thus, if m and m' be the number of gramme equivalents of the two substances A and B present in the unit volume of the solution, the speed of the reaction would be measured by $k \times m \times m'$ where k is a constant. It is obvious that other things being uniform the rapidity of a reaction will depend upon the frequency of collisions between substances which are to react. If the number of equivalents m of one substance be doubled the number of collisions per unit time between the molecules of A with those of B will be doubled. So, too, if m' be also doubled, the number of collisions per unit time will be again doubled, so that the speed of the reaction will now be represented by $k \times 2m \times 2m'$, *i.e.*, four times as great as before.

If one of the substances is insoluble in water (or so little soluble that there is always some of it present in the solid state) its active mass is constant and the speed of the reaction then varies only as the active mass of the soluble substance varies.

Now when two substances react they, as a rule, form two other substances, which may react upon each other, re-forming the original two. This occurs in all so-called reversible reactions. In such cases equilibrium is attained when the speeds of the reaction in the two directions are equal. Consider the case to which allusion has already been made and let a = number of equivalents of K_2CO_3 per unit volume, b the active mass of $BaSO_4$ (constant because insoluble), c the number of equivalents of K_2SO_4, and d = the active mass of $BaCO_3$ (again constant). Then the condition for equilibrium would be—

$$k\ (a-x)\ (b-x) = k'\ (c+x)\ (d+x)$$

but since b and d are constant they are not altered by the subtraction or addition of x, which represents the number of equivalents of K_2CO_3 (or $BaSO_4$), which undergoes the change.

Hence the equation may be written—

$$k\ (a-x)\ (b) = k'\ (c+x)\ (d)$$

$$\therefore\ \frac{k}{k'} = \frac{(c+x)\ d}{(a-x)\ b}$$

or if single equivalents were taken of K_2CO_3 and $BaSO_4$

$$k\ (1-x)\ (b) = k'\ x\ d$$

$$i.e.,\ \frac{k}{k'} = \frac{x\ d}{(1-x)\ b}$$

and since $\frac{d}{b}$ is constant, we see that equilibrium is reached when $\frac{x}{1-x}$ attains a certain value.

This result means that equilibrium is attained when the ratio of potassium sulphate to potassium carbonate reaches a certain fixed value.

The same is true (with different values for the ratio) with all other reactions of similar type where there are two soluble and two little soluble or insoluble substances concerned. It applies, for example, to a change which is often made use of in agricultural practice and affords an explanation of what may appear puzzling and contradictory to the student. Calcium sulphate is used as a means of lessening the loss of ammonium compounds from manure heaps; this it is said to do by undergoing double decomposition with the volatile ammonium carbonate yielding non-volatile ammonium sulphate and calcium carbonate.

On the other hand, when ammonium sulphate is applied as a manure to a soil, calcium sulphate is found in the drainage water and ammonium carbonate is apparently held back in the soil until nitrification occurs.

As represented in the ordinary text-book manner the reactions are:—

In the case of the manure heap—

$$CaSO_4+(NH_4)_2CO_3=CaCO_3+(NH_4)_2SO_4$$

and in the case of ammonium sulphate applied to soil—

$$CaCO_3+(NH_4)_2SO_4=CaSO_4+(NH_4)_2CO_3.$$

Now, in the light of what has been said, it is obvious that neither of the equations really represents what happens in either case,

In the first place the carbonates involved in the reactions are probably not normal carbonates but acid carbonates, since excess of carbon dioxide is present both in the manure heap and in the soil.

The reaction might be represented—

$$CaSO_4+2NH_4HCO_3 \rightleftarrows Ca\ (HCO_3)_2+(NH_4)_2SO_4$$

equilibrium being attained when the ratio of the ammonium sulphate to the ammonium carbonate attains a certain value if the solutions are so concentrated that separation of $CaSO_4$ and $Ca(HCO_3)_2$ in the solid state can occur (as perhaps may happen in a manure heap); but the conditions of equilibrium will, in dilute solution, be also affected by the quantities of calcium sulphate and calcium bicarbonate present in a dissolved state, for it must be remembered that their influence only becomes constant when they are present in such quantities that they separate partially in the solid state.

It is only fair to say, however, that the tendency for the soil to absorb and retain ammonium carbonate will also play an important part in the case of the action in the soil, that compound being withdrawn from the sphere of action as fast as it is formed, thus diminishing the speed of the reaction represented by the equation read from left to right.

CHAPTER V.

THE ANALYSIS OF SOILS.

IN this chapter only a brief outline of the methods of sampling and analysing soil will be given. For full details a treatise on soil analysis should be consulted. The methods described here are such as the author himself uses, and variations may be made in them to suit special cases.

Sampling.—This is an important operation, and careful consideration should be given to it. Much depends upon the particular object for which the analysis is to be made. If it be desired to report upon the soil of a farm or field as a whole, and much difference exists in the soil from different parts of it, care must be taken that in the final sample, each different soil should be represented, as far as possible, by a quantity bearing a proportion to the total sample equal to the proportion (of the whole area) covered by that particular soil. Better knowledge of the nature of the soil, however, is obtained if samples presenting notable differences be kept apart and analysed separately.

Then, too, the depth to which the samples are taken is a matter for consideration. Generally speaking, the samples should be taken down to the line of separation of the soil from the subsoil, which is often very clearly visible by a difference in colour, the soil proper being darker (because of organic matter) than the subsoil. The depth is usually from 6 to 10 inches. In many cases it is required to also examine the subsoil, when, of course, separate samples must be collected.

Of the various methods of taking the samples the following may be mentioned:—

(1) Having selected the place, the vegetation growing upon it is removed and a hole is dug with a sharp spade to a depth of about 12 inches, one side (of the hole) being trimmed so as to be quite smooth and perpendicular.

A slice from this side is then cut with the spade to a suitable depth and about 3 or 4 inches in thickness. This is placed on a clean board to be mixed with the other samples obtained in a similar way from other parts of the field. Finally, these sub-samples are mixed together thoroughly with a trowel or the spade, the sticks, large stones, and roots being removed, and a sample of 2 or 3 kilograms taken for analysis.

(2) Another, more laborious, plan is to have wooden boxes 6 inches square and 12 inches in depth to hold the samples. A large hole is then dug at the selected spot and a square prism of soil is left in the centre; this is carefully trimmed with the spade until the box will just slip over it. The surface of the prism is freed from vegetation, the box is inverted over it, and by means of the spade the box with the column of soil is removed, a label giving particulars of the sample put in, and the lid screwed on. A sample of the soil and subsoil *in situ* is thus obtained which can be further treated in the laboratory. Several of such samples can be united before a final sample is taken.

(3) A quicker and in many ways a satisfactory method of sampling consists in taking specimens by means of a 2 or 2½ inch auger, the borings being placed on a board, a number of them (a dozen or more) from various parts of the area to be examined being mixed together and taken for analysis. A board about 2′ 6″ × 1′ 3″, with a hole in it just large enough to easily pass the auger, will be found convenient to stand upon and also to receive the borings.

For general purposes a chemical analysis of the soil is all that is usually done, but great importance is undoubtedly to be attached to its physical properties (*e.g.*, specific gravity, real and apparent, specific heat, conductivity for heat, absorptive power for salts and for water, size of particles, capillarity), and in America and Germany soils are examined with a view to determining these properties and expressing them quantitatively; but for methods the student is referred to the writings of Knop, Kœnig, and Wiley. It is usual to submit the soil to a rough mechanical analysis before commencing the chemical analysis.

Mechanical Analysis.—The soil collected in its damp state is first air-dried. This is done by spreading it on paper and exposing to air for some days, care being taken to exclude dust, products of combustion or other foreign matters. In order to increase the rate of drying, the author has used a glass chamber provided with shelves, from which air is drawn by a fan, driven by an electric motor, the necessary supply of fresh air being admitted at the bottom, after being warmed by passing over resistance coils (used for diminishing the current supplied to the motor) and filtered through calico. In this way air at a temperature of 25° to 30° C. is drawn over the soil and drying is completed in a short time. Before the soil is thoroughly dry it is rubbed between the hands or with a wooden or rubber-covered pestle, in order to crumble it to powder, care being taken not to crush stones or mineral fragments. When dry a convenient quantity, 1 or 2 kilograms, is weighed out and passed through a sieve having meshes 3mm. or ⅛in. diameter (best made of metal with circular perforations). The portion failing to pass this is subjected again to hand rubbing until no aggregations of clay, &c., are left. Finally, the stones retained by the 3mm. sieve are removed and weighed, the portion passing through is stored in a stoppered bottle for the chemical analysis and duly labelled, the percentage of stones removed being conveniently recorded on the label.

It is rarely desirable to make an analysis of the stones, though in a thorough examination of a soil their character and probable composition should be recorded.

Further mechanical analysis of the portion passing the 3mm. sieve is sometimes performed, depending upon its separation (i.) by sieves of suitable mesh and (ii.) by elutriation, *i.e.*, washing in a current of water of suitable strength and allowing the turbid liquid to settle.

By the sieve method it is not advisable to attempt any further sub-division than is given by holes ·5mm. in diameter. Sieves of 3mm., 1mm., and ·5mm. holes are sufficient for most purposes, thus dividing the soil into four parts. If further separation is desired, elutriation must be resorted to, for details of which a treatise on soil analysis should be consulted.

In some cases a microscopical examination of the various sediments is made in order to determine their mineralogical nature. For a purely chemical examination a sieve of 3mm. and one of 1mm. perforations (practically $\frac{1}{8}$in. and $\frac{1}{25}$in.) are all that are necessary.

Chemical Analysis.—A full chemical analysis of a soil, including the determination of the quantities of every ingredient, is rarely required. If it be, the "fine soil" passing the 3mm. sieve is reduced to fine powder, the particles of which are, at least, able to pass the 1mm. sieve.

Determination of Moisture.—About 5 grammes of the air-dried fine soil which has passed the 1mm. sieve are accurately weighed in a flat-bottomed platinum dish previously weighed with a short piece of stout platinum wire to act as stirrer. The dish is heated to 100° in a steam bath for 12 hours, with occasional stirring of its contents. It is then cooled in a desiccator and weighed, again heated for an hour, and re-weighed. If the difference between the two weighings does not exceed 2mgm. the moisture is calculated from the loss in weight If the difference between the two weighings exceeds 2mgm. the dish is again heated for an hour at 100° and re-weighed until two successive weighings show less difference.

Determination of Loss on Ignition.—The residue from the moisture determination is heated to low redness, with occasional stirring, until all black particles are destroyed. This can very conveniently be done in a muffle furnace. The dish is removed, allowed to cool, the contents moistened with ammonium carbonate solution, dried, heated to about 150°, or even to low redness for a minute or two, again cooled and weighed. The loss is equal to the organic matter and combined water. The object of the treatment* with ammonium carbonate is to restore any calcium carbonate (which would be decomposed by the heating into carbon dioxide, which would escape, and quick-lime) back into its original form. Otherwise the loss on ignition would include the carbon dioxide thus expelled.

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* Several errors in the determination of moisture are not adequately corrected for by this treatment;—magnesia left from magnesium carbonate on ignition only very slowly takes up carbon dioxide again; so, too, lime present as calcium humate will be converted into carbonate. These errors and others inherent in the method are small and can usually be ignored.

Care must be taken that the temperature be as low as is consistent with the oxidation of the carbon, or loss, due to volatilisation of alkaline chlorides, may occur.

Determination of Nitrogen.—The nitrogen in a soil may exist in three states of combination :—

1. As nitrates.
2. As ammonium compounds.
3. As organic compounds of complex but little known constitution, associated with the "humus."

The nitrogen existing at any given time in a soil in the state of nitric acid or ammonia is usually very small in amount and in most cases does not require separate determination.

Total Nitrogen.—Several methods are in use for the determination of nitrogen in soil, but of recent years the well-known Kjeldahl process for the determination of nitrogen in organic substances generally, has, with various modifications in detail, been adopted in soil analysis.

Broadly speaking, the method is based upon the behaviour of strong sulphuric acid towards organic matter; by continued heating with strong acid the carbonaceous matter is oxidised into carbon dioxide and water, the nitrogen which it contains being converted into ammonia, which in the presence of the large excess of acid, remains behind as ammonium sulphate. A large proportion of the sulphuric acid is reduced with the evolution of sulphur dioxide. It is found that the oxidation of the organic matter is facilitated by the addition of small quantities of certain metallic salts, *e.g.*, of mercury or copper. They apparently act as carriers of oxygen from the acid to the organic matter.

The following are the details of the method which the author uses :—

10 to 15 grammes of the air-dried "fine soil" (*i.e.*, which has been crushed and passed a 1mm. sieve) are introduced into a 16oz. spherical flask and treated with 20 to 25 c.c. of *pure* sulphuric acid (which must be free from ammonia, the

re-distilled acid of commerce is usually pure enough), heated for some time over the bare flame, care being taken that the soil is completely wetted by the acid and that no dry places are left in the lower part of the flask. When the frothing has ceased (usually in about half an hour) 10 grammes of pure potassium sulphate are added to the flask and about half a gramme to a gramme of anhydrous copper sulphate (easily prepared by heating powdered blue vitriol in a porcelain basin until it becomes quite white); the heating is then continued in the draught place, the flask being either placed in an inclined position or a small funnel or watch glass being placed on its neck in order to prevent loss by spirting. The contents of the flask should be kept in constant ebullition, due care being taken to avoid frothing over, which may occur in the early stages of the heating. The flask is best supported upon a retort-stand ring, its neck passing through a smaller ring, and it is advisable to periodically rotate the flask so that no fragments of soil may escape the action of the acid, or rather of the acid potassium sulphate.* When all black or brown colouration disappears (generally in about 1½ to 2 hours from the time of starting the heating) it is safe to assume that the reaction is completed. The flask is then allowed to cool, about 50 c.c. or more of distilled water added, and a cork carrying a separating funnel, delivery tube, and inlet tube for steam is inserted, the arrangement being shown in the diagram. In the separating funnel is placed about 80 or 90 c.c. of strong caustic potash solution made by dissolving "stick" potash in its own weight of water and boiling the solution for some time to expel any possible ammonia. This solution can be prepared in considerable quantities and kept in a closely corked bottle.

When the apparatus is fitted up as described, a measured quantity—25 c.c.—of decinormal sulphuric acid is run from a pipette into F through G, the cork being loosened to allow of the escape of air. B should be disconnected from A at the rubber joint R and the water in B heated to boiling. In the meantime the 80 or 90 c.c. of potash solution in C are

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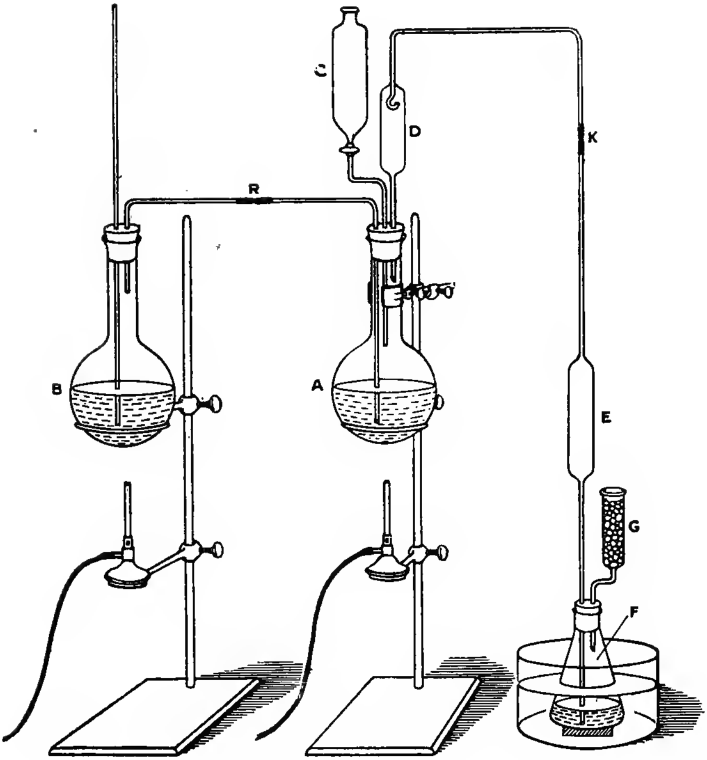
* The object of adding the potassium sulphate is to allow the temperature to be raised to a higher point than is possible with sulphuric acid alone. Indeed, the liquid in the flask at the end consists essentially of fused potassium hydrogen sulphate.



A is the flask in which the soil has been heated with the sulphuric acid.

B is a similar flask containing water and a scrap of granulated zinc so as to ensure a steady evolution of steam. This flask is fitted with a safety tube so that the pressure in the apparatus can be determined at once (by the height of the water in this tube).

C is a separating funnel, bent so as to fit properly and containing the strong potash solution.

D is a bulb on the delivery tube, with an arrangement for preventing any particles of the solution in A from being carried over by the steam.

E is a 50 or 100 c.c. pipette, which acts as a condenser to some extent and prevents any standard acid being drawn back if the evolution of steam be suddenly stopped.

F is an 8oz. conical flask.

G is a tube shaped as shown and filled with glass beads through which the standard acid has been allowed to run into F.

allowed to trickle slowly and with frequent shaking, or better, rotation, into A. The copper sulphate affords a good indication of the amount required. When the solution is alkaline the copper is precipitated as blue copper hydroxide, which, however, is usually quickly converted into black copper oxide owing to the heat evolved by the action of the potash on the sulphuric acid. Care should be exercised, lest frothing takes place during neutralisation. When an excess of potash has been added, the tap of the separating funnel is turned off and steam from B is admitted by connecting with the rubber tube at R. The lamp under A should only have a small flame, lest bumping, due to the presence of the solid matter in the flask, be produced. The flame under B should be of such a size that the pressure of the steam is sufficient to raise the water in the vertical tube some 8 or 10 inches, due attention being, particularly at first, directed to the prevention of frothing in A. The flask F should be surrounded with cold water in order to condense the steam coming over. This method works very satisfactorily and the ammonia is entirely driven over in about half an hour, and there is little risk of bumping or sucking back.

When the operation is over, the rubber at K is disconnected, the cork loosened from F, E and G are rinsed out by distilled water into F, a little (one or two drops) methyl orange solution added, and decinormal caustic soda solution added from a burette until the red colour just disappears. The amount of ammonia and hence of nitrogen is then easily calculated from the amount of sulphuric acid which has been neutralised by the ammonia carried over in the steam.

The method gives the nitrogen existing as organic matter and as ammonia in the soil; it also probably gives some at least of that existing as nitrates, but if nitrates are likely to be present in any considerable quantity about a gramme of salicylic acid or benzoic acid should be added with the sulphuric acid, when nitro-compounds of these acids will be formed, readily capable of reduction to amides and finally to ammonia.

An example will show the method of calculation. 10·868 grammes of soil were treated as described. On distillation into 50 c.c. of decinormal sulphuric acid there were required afterwards 27·0 c.c. of decinormal sodium hydrate solution. Hence 50 − 27·0 = 23 c.c. of the acid must have been neutralised by the ammonia. 1 c.c. of decinormal sulphuric acid contains ·0049 gramme of real H_2SO_4, equivalent to neutralising ·0017 gramme of ammonia, corresponding to ·0014 gramme of nitrogen. Hence the 27 c.c. of sulphuric acid correspond to 23 × ·0014 gramme of nitrogen, and this was present in 10·868 grammes of soil.

The percentage of nitrogen is therefore—

$$\frac{23 \times \cdot0014 \times 100}{10\cdot868} = 0\cdot270\,\%\text{ nitrogen.}$$

Direct estimation of humus.—A method originally proposed by Grandeau* is based upon the solubility of humus in ammonia. About 10 grammes of the soil are treated with dilute hydrochloric acid (containing about 1 % real acid) until all lime and magnesia are removed. Then the acid is washed out by water and the soil residue is treated with about 15 c.c. of ammonia (strong ammonia diluted with about its own volume of water) for three or four hours; the whole is then filtered and the residue washed once or twice with dilute ammonia. The dark-coloured solution is then evaporated in a weighed platinum dish, dried at 100°, and weighed. The contents of the dish are then ignited and the organic matter thus oxidised. The loss of weight on ignition is the amount of humus. The phosphoric acid in the residue may be determined in the usual way, and, according to Grandeau, affords a good measure of the available phosphoric acid of the soil.

Determination of the silica, alumina, ferric oxide and *total potash.*—3 or 4 grammes of the finely divided soil are weighed out accurately into a conical flask, 20 c.c. of strong hydrochloric acid are added, and the whole boiled on a sand tray for 10 minutes, a watch glass being placed on the neck of the flask to prevent loss by spirting; the flask is then placed on the steam bath and digested at 100° C. for 48 hours. The liquid is then diluted and filtered, the residue washed with hot water, dried, ignited, and weighed.

This is reported as silica, though in many cases it doubtless still contains some refractory silicates. The filtrate and washings are evaporated to complete dryness in a platinum or porcelain basin on the water bath, the residue heated over a flame until thoroughly dry and the organic matter charred or burnt, cooled, moistened with strong hydrochloric acid, taken up with water, and filtered; the residue is ignited and weighed, its weight, "soluble silica," being added to the other "silica" already separated.

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* *v.* "Analyse des Matières Agricoles," 1897, Vol. I., 141.

The filtrate and washings are made up to 100 c.c. (or 250 if more convenient). 25 c.c. (or 50 if from 250 c.c.) are then taken, boiled with a few drops of nitric acid, in order to oxidise the iron, and mixed with just sufficient ammonia to neutralise the free acids present. A slight excess of ammonia is then added and the whole boiled until the free ammonia is nearly all expelled. The precipitate is filtered off, washed, thoroughly dried, ignited, and weighed. The weight is equal to the ferric oxide, alumina, and phosphoric acid present.

Another portion of the filtrate from the silica is taken for the determination of the total potash. This can be done conveniently and accurately by Tatlock's method.

25 c.c. (or 50 c.c.) of the hydrochloric acid solution are placed in a porcelain dish, and platinum tetrachloride in sufficient quantity to convert all the potash, soda, and magnesia into double chlorides is added (in general, about ·3 gramme will be sufficient), and the liquid slowly evaporated on the water bath. The residue is washed, first with a little platinum chloride solution, which dissolves and removes sulphates, phosphates, &c., also the double chlorides of platinum with calcium, sodium, magnesium, &c., and then by decantation, in the dish, with alcohol (96 %, not methylated), the washings being passed through a small filter. When the washings are colourless, the precipitate, which should consist of bright orange crystals, is washed with alcohol into a weighed porcelain crucible, and the alcohol poured off as completely as possible through the filter. The crucible is then placed in a warm place for a short time, heated in a steam bath for two hours, and then weighed. The small filter, which should only contain traces of precipitate, is then burnt in platinum wire, its ash added to the crucible, and the whole again weighed. The last increase is taken as being due to $2KCl+Pt$. It is calculated to K_2PtCl_6

and added to the weight of the main quantity of the precipitate. From the sum of these weights the amount of potash in the soil can be calculated, knowing that 94 of potash (K_2O) correspond to every 485 of the double chloride.

This method works very well and is a great saving in time and labour over the old methods requiring the preliminary removal of the iron, aluminum, lime, and magnesium. Unfortunately it prevents the simultaneous determination of the sodium.

The so-called "total potash" obtained in this way is not necessarily the whole quantity of potash which the soil contains, for hydrochloric acid does not remove all the potash from silicates.

If the real total potash be required, it is necessary to analyse the residue insoluble in hydrochloric acid, exactly as is done with a mineral silicate. However, the potash in a soil insoluble in hydrochloric acid is probably unavailable to plants for many years to come, so that its determination is not often of importance.

Determination of "total" phosphoric acid.—This can conveniently be done in the portion of the soil taken for determination of loss on ignition. The residue in the platinum dish is treated with strong hydrochloric acid, digested for some time, evaporated to dryness, and heated to render the silica insoluble, moistened with strong hydrochloric acid, taken up with water, filtered, and evaporated with strong nitric acid. It is again diluted and mixed with excess of ammonium molybdate solution and allowed to stand in a warm place for 18 or 24 hours. It is then filtered, washed by decantation with dilute nitric acid and once with water, then dissolved in dilute ammonia (filtered if necessary), mixed with "magnesia mixture,"* and allowed to stand 12 hours. The ammonium magnesium phosphate, NH_4MgPO_4, is then filtered off, washed with ammonia, dried, ignited slowly and carefully, and weighed as $Mg_2P_2O_7$. Phosphoric acid may also be determined in a portion of the hydrochloric extract of the soil.

Determination of the lime and magnesia.—Except in some few cases, the amount of these constituents is so small that they cannot be accurately determined in the three or four grammes of soil taken for the previous determinations, especially as at least half of the solution will have been used for determinations of iron and alumina and total potash.

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* A solution containing magnesium chloride, ammonium chloride, and ammonia.

It is usually advisable, therefore, to take 6 or 8 grammes of soil, treat and digest with hydrochloric acid as before, remove the silica, ferric oxide, alumina, and phosphoric acid as before from the whole solution, then to the filtrate from ferric oxide, &c., to add ammonium oxalate, allow to stand twelve hours, filter, wash, dry, ignite in platinum crucible to constant weight, and weigh as calcium oxide.

The filtrate from the calcium oxalate is freed from ammonium salts by evaporation with nitric acid in the usual manner and the magnesium precipitated as ammonium magnesium phosphate and weighed as magnesium pyrophosphate.

Determination of the amount of calcium carbonate.—A direct determination of the amount of carbon dioxide evolved on treatment with dilute hydrochloric acid is sometimes advisable, since for many purposes the lime existing as carbonate is of more importance (as regards nitrification, for example) than the total lime, some of which may be as silicate. This can be done by any of the usual methods, either receiving the evolved gas in weighed potash bulbs; or, if its amount be large, by determining the loss in weight of an apparatus in which it is generated and from which it can be wholly removed by a current of air. Details of these methods will be found in any manual of quantitative analysis.

A complete chemical analysis, though of service as giving the limits of the plant food which a soil can provide, is often of disappointingly little use and frequently affords no information of value as to fertility or manurial requirements.

A good example of such failure is seen in the following analyses of two soils from pasture land at the Experimental Farm at Garforth made by the author in June, 1900:—

"Fine-soil" contains—

	Soil A.	Soil B.
Moisture	3·13	1·70
Loss on ignition	10·85	7·79
(Nitrogen	·274	·247)

	Soil A.	Soil B.
Insoluble matter	67·38	80·28
Ferric oxide and alumina (Fe_2O_3 and Al_2O_3)	15·61	8·16
Lime (CaO)	·29	·13
Magnesia (MgO)	·31	·21
Potash (K_2O)	·86	·48
Phosphoric acid (P_2O_5)	·15	·12
Not determined (soda, chlorine, &c.) ...	1·42	1·13
	100·00	100·00

From these figures it would appear that soil A is better provided with lime, potassium, and phosphoric acid than soil B, and inasmuch as there is also more nitrogen present one would conclude that soil B would receive much more help from phosphatic and lime manures than soil A.

Actual practice shows exactly the opposite, for it is found that basic slag produces a large increase and great improvement in the crop on the field from which soil A was taken, while the field from which soil B was derived does not respond to applications of basic slag.

From such disagreements between the results of chemical analysis and actual farming experience, which are often met with, it is evident that to know what a soil contains is not sufficient to enable one to form a judgment as to its fertility; one must know, in addition, something about the state of existence of the important items of plant food—must know, in fact, *the amounts of these which are directly available to the plant.*

Many methods of extracting soil so as to obtain some measure of the phosphoric acid and potash particularly, which are in an assimilable form, have been suggested. One of the most successful is that of Dyer.* This method is based upon the extraction of the soil with a one per cent. solution of citric acid, which Dyer found to be about the average acidity of the juices of the roots and root hairs of a large number of plants examined by him.

The method is thus carried out: 200 grammes of the air-dried soil which has passed the 3mm. sieve are, without further treatment, placed in a flask or bottle, and treated with 2000 c.c. of water containing 20 grammes of pure crystallised citric acid. The two are left in contact, with frequent stirring or shaking, for seven days, at the ordinary temperature of the laboratory. The liquid is then filtered, best through a Buchner's "nutschen" or porcelain funnel with parallel sides and perforated base, by the aid of a filter pump. 500 c.c. of the filtrate are taken for the determination of the available potash and a like quantity for the available phosphoric acid.

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* Jour. Chem. Soc. 1894, Trans. 141.

These two portions are evaporated to dryness and gently ignited to destroy organic matters. The potash and phosphoric acid are then determined exactly as already described.

That this method of determining the available potash and phosphoric acid affords valuable help in judging of probable fertility is shown by its application to the two soils whose analyses have been given.

The results were as follows:—

	Soil A.	Soil B.
Available potash ...	·0062 %	·0060 %
Available phosphoric acid...	·0049 %	·0205 %

It is thus evident that so far as potash is concerned the two soils are almost alike, but that soil A, though containing more total phosphoric acid than B, contains less than one-fourth as much in an available form. The beneficial effects of basic slag on soil A is thus easily understood, soil B containing an abundance of available phosphates.

Dyer points out *that less than ·01 % of available phosphoric acid in a soil indicates that it stands in immediate need of phosphatic manures.* With reference to the limit for the available potash, Dyer thinks, though he expresses more doubt in this case than with the phosphoric acid, that *soils containing much less than ·005 % available potash require application of potash manures.*[*]

A few other constituents may require determination for special purposes:—

Determination of sulphuric acid.—Sulphur is found in a soil as sulphates (most frequently calcium sulphate), in organic compounds, and occasionally also as sulphides (*e.g.*, iron pyrites). The sulphuric acid, existing as such, may be determined by digestion of the soil with dilute hydrochloric acid, filtration, and precipitation of the solution with barium chloride in the usual way employed for sulphuric acid determinations. The total sulphur may be sufficiently well determined by digestion with concentrated nitric acid for six hours, diluting with water, filtering, and precipitating the filtrate with barium chloride.

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[*] In a subsequent paper (Proc. Roy. Soc. 1901, 11) Dyer states that for cereals the limit denoting deficiency in phosphoric acid is between 0·01 and 0·03 % soluble in 1 % citric acid solution. In root crops, especially turnips, the limit would probably be higher. He also states that soils containing 0·01 % of potassium soluble in 1 % citric acid probably require no further application of potash manures.

Determination of nitrates.—The amount of nitrate present in a soil at any given time is usually very small and it is not, as a rule, necessary to determine it.

Sometimes, however, a determination is made for special purposes.

If such be required it is important that the soil be air-dried as soon after its collection as possible, otherwise the process of nitrification may continue and increase the amount of nitrates. It is advisable to accelerate the process of drying by heating the soil to 30° or 40° C. and drawing a current of warm air over it. An arrangement which the author finds very convenient for drying soils before analysis is described on p. 91. With this apparatus the operation can be rapidly completed without the possibility of contamination by dust, products of combustion, &c., and with little opportunity for nitrification to appreciably increase the quantity of nitrates in the soil.

From the air-dried soil the nitrates are extracted by washing with water. Many methods may be used :—

(1) 1000 grammes are treated with 2 litres of pure water and allowed to stand for 48 hours, with occasional shaking. 1 litre of the liquid is then filtered, mixed with a little pure sodium carbonate, and evaporated to small volume on the water-bath, any precipitate which may form being removed by filtration.

(2) A cylindrical funnel is made by removing the bottom from a "Winchester quart" bottle, placing a disc of copper gauze on the shoulder, and covering this with two filter papers. The bottle is then connected by means of a cork and tube to a filtering flask and from 200 to 500

grammes of dried soil are placed in it, resting on the paper-covered wire gauze. Water is then poured in until the whole of the soil is moistened, small quantities of water are added from time to time, and the filter pump started gently. When 100 c.c. have percolated it may be assumed that all the nitrates are removed (Warington).

In the extract obtained, the amount of nitric nitrogen may be determined by one of the following methods:—

(1) *The reduction of the nitric acid to nitric oxide and the measurement of the volume of this gas.*

This can be effected either by—

Schloesing's method, in which the nitrate is treated with ferrous chloride and strong hydrochloric acid—

$$6FeCl_2+2KNO_3+8HCl=6FeCl_3+2KCl+4H_2O+2NO.$$

Crum-Frankland's method, in which by the action of metallic mercury and sulphuric acid the nitrate yields its nitrogen as nitric oxide—

$$6Hg+4H_2SO_4+2KNO_3=3Hg_2SO_4+K_2SO_4 \\ +4H_2O+2NO.$$

This latter method is vitiated if any appreciable quantity of organic matter be present. The former method gives good results, even in the presence of organic matter. The Crum-Frankland method can be conveniently carried out in Lunge's nitrometer, for a description of which any treatise on quantitative analysis may be consulted.

(2) *The decolorisation of a solution of indigo by the nitrate in the presence of sulphuric acid.*

The amount of nitric acid is then estimated by comparison with the quantity of a solution of potassium nitrate of known strength required to decolorise an equal volume of the same indigo solution, under similar conditions of temperature and concentration.

This process is also subject to interference by the presence of organic matter and is now rarely used for soils.

(3) *The reduction of the nitrates to ammonia and the subsequent determination of the amount of ammonia so formed.*

This reduction is brought about by the action of nascent hydrogen, which may be generated by—

(a) An oxidisable metal in presence of an alkali.
(b) Action of a metal on an acid.
(c) Electrolysis of water.

In all cases the main chemical reaction is the same—

$$HNO_3 + 4H_2 = NH_3 + 3H_2O$$

—one molecule of ammonia being formed from one molecule of nitric acid.

The ammonia formed is then estimated by distillation with an alkali and reception in a measured quantity of standard acid, the amount of acid neutralised being afterwards determined by titration with standard sodium hydrate exactly as in the Kjeldahl process for total nitrogen.

In some cases, where the quantity of nitrate present is small, the amount of ammonia formed is estimated by the well-known Nessler's method as used in water analysis.

Many variations in this process have been devised. Thus, as reducing agents the following have been used: sodium amalgam containing about ·5% sodium, alloy of aluminium, copper and zinc in fine powder, the copper-zinc couple, the aluminium-mercury couple, zinc or iron dust, aluminium powder; these are all applied in alkaline or neutral solution. In acid solution, iron or zinc dust may be employed either in the presence of acetic, or more generally, sulphuric acid.

In all these cases, after the reduction of the nitrate to ammonia is complete, an operation which goes most quickly, as a rule, in the acid solutions, a large excess of caustic soda or potash is added and the whole distilled, the ammonia being received in sulphuric acid, in which its amount is determined by titration, if it be large, or by Nesslerisation, if it be small.

(4) *The production of a colour with certain organic substances in presence of sulphuric acid and the comparison of the depth of colour produced with that formed by a known amount of pure potassium nitrate under like conditions.*

Many substances have been used for the purpose of yielding the colour—thus, carbazole or diphenylimide, $\left.\begin{array}{l}C_6H_4\\C_6H_4\end{array}\right\}NH$,—phenyl-sulphuric acid, $C_6H_5HSO_4$,—brucine, $C_{23}H_{26}N_2O_4.4H_2O$.

In the case of carbazole, an acetic acid solution of the substance is added to pure sulphuric acid. The mixture gives, when added to a liquid containing a nitrate even in minute quantities, a deep green colouration, the intensity of which is compared with that given with a solution of potassium nitrate of known strength after the manner of Nessler's ammonia process. This reaction is only reliable in the absence of chlorides and iron compounds. These have, therefore, to be removed from the soil extract.

Phenyl sulphuric acid is converted into picric acid by nitrates and the ammonium picrate formed on the subsequent addition of ammonia is possessed of a strong yellow colour.

The reaction is—

$$\underset{\text{Phenyl sulphuric acid.}}{C_6H_5HSO_4} + 3HNO_3 = \underset{\text{Picric acid.}}{C_6H_2(NO_2)_3OH} + H_2SO_4 + 2H_2O$$

and on the addition of ammonia—

$$C_6H_2(NO_2)_3OH + NH_4OH = C_6H_2(NO_2)_3ONH_4 + H_2O.$$

Brucine gives with a nitrate in the presence of strong sulphuric acid an intense red colouration.

In all cases these reactions are applicable to the determination of minute quantities of nitrates, and it is obvious that only the purest reagents must be employed.

If a determination of ammonium salts in a soil be desired, distillation of a weighed quantity of the soil with pure water and magnesia is performed, the ammonia evolved being received in standard sulphuric acid. Magnesia is employed instead of soda or potash because it has not, like these alkalis, the power of setting free a portion of the nitrogen (as ammonia) from organic nitrogenous compounds.

Determination of nitrites.—Nitrites are, as has been shown in Chap. IV., an intermediate stage in the conversion of organic or ammoniacal nitrogen into nitrates. Their presence in a soil may sometimes be detected, but only minute quantities are usually present unless the activity of the nitric organism is not so great as that of the nitrous organism.

Many delicate reactions, mainly colorimetric ones, can be used for their detection and estimation. Metaphenylene diamine, $C_6H_4(NH_2)_2$, gives with nitrous acid an intense yellow colouration, and this colouration, developed by heating, is compared with that obtained by the use of a known quantity of a nitrite.

A more delicate test, not so readily interfered with by the yellow colour which the soil extract may possess, is the addition of a mixture of sulphanilic acid and naphthylamine in acetic acid.[*] This gives with minute traces of nitrites, when warmed to 70° or 80°, a red colouration.

The reaction is due to the following changes:—

$$C_6H_4NH_2HSO_3 + HNO_2 = C_6H_4\left\{\begin{matrix}N:N\\SO_3\end{matrix}\right\} + 2H_2O$$

p-amido benzene sulphonic acid or sulphanilic acid.

p-diazo benzene sulphonic acid.

$$C_6H_4N_2SO_3 + C_{10}H_7NH_3C_2H_3O_2$$

a-naphthylamine or naphthylammonium acetate.

$$= C_{10}H_6NH_2.N:N.C_6H_4HSO_3 + HC_2H_3O_2$$

a-amido naphthalene azo-benzene *p*-sulphonic acid.

This complex compound has intense tinctorial power and is the cause of the red colouration.

Another reaction for nitrites of considerable delicacy, though liable to interference by the presence of organic matter, is the liberation of iodine from hydriodic acid and its detection by the formation of the blue colour with starch.

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[*] Griess, Zeits. für analyt. Chem. 18, 597.

CHAPTER VI.

NATURAL MANURES.

FROM what has been said in Chapters III., IV., and V., it is evident that the fertility of a soil depends upon a number of circumstances; among others, upon the existence of suitable relationships between its properties regarded from—

(1) Mechanical
(2) Chemical
(3) Biological

points of view.

(1) The possession of the proper fineness of sub-division, porosity, water-holding power, and other physical properties is essential to permit of the ready growth of a plant's roots, to afford the necessary mechanical support and access of air to the roots, and to provide them with a due supply of moisture. If these properties are lacking, no matter how rich the soil may be, it cannot possess, in the highest degree, true fertility.

(2) So, too, from a chemical standpoint, the possession of a suitable store of plant food in an available condition is obviously necessary. If the plant food, or any part of it, be present in insufficient amount, or in a completely insoluble or unavailable form, the soil, however suitable in mechanical structure, must be incapable of yielding the best results.

(3) The conversion of one of the most important constituents of plant food, nitrogen, from a state of combination in the insoluble, highly complex, organic substances associated with humus into the directly assimilable nitrates, is, as already described (Chap. IV.), accomplished by the action of micro-organisms, so that it is evident that the realisation of one of the above conditions—as to availability of plant food in the soil—can only be effected if

the necessary micro-organisms or their spores are present. Even more dependent upon the presence of suitable micro-organisms is the utilisation of the free atmospheric nitrogen by the leguminosæ. Fungi, yeasts, other low forms of life, as well as worms, caterpillars, larvæ, &c., also play an important part in altering both the physical and chemical properties of soil. Unfortunately, in the case of the latter organisms, their influence on the plant itself often exceeds in importance their effect on the soil.

Improvements in the soil are naturally the aim of the agriculturist. As regards its physical condition, much can be done by tillage operations—ploughing, harrowing, draining, &c.—also by the introduction of materials which affect the mechanical properties of its constituents, *e.g.*, lime, bulky vegetable refuse, &c.

With reference to the actual plant food in a soil, improvements can be effected in two ways—

(1) The addition of substances containing plant food.

(2) The addition of substances which may act upon the insoluble compounds present in the soil and render available the plant food they contain.

As to improvement in its biological qualities little has hitherto been done, but in the future, probably, this may be a direction from which considerable help may be derived.

The destruction of insect pests, and the eradication of organisms producing diseases in crops or in animals feeding upon the land, are problems which have already been studied with some success. A certain amount of progress, too, has been made in devising means for inoculating the soil or seed with desirable micro-organisms, as witness the commercial production of "alinit" and "nitragin."* Proposals to regulate nitrification by the application of antiseptics, so as to lessen the autumnal loss of nitrates in the drainage, have been made;† but, so far as the author is aware, these methods have not sufficiently commended themselves to the practical farmer to be adopted to any extent on the large scale.

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* See pages 80 and 81.

† Dehérain, *v.* p. 68.

It is with the improvements in the chemical state of the soil that this chapter has mainly to deal.

These are effected by the application of **Manures.** The word manure has apparently a connection with the Latin *manus*—a hand—and was probably used because of an old belief that the main function of a manure was, by its fermentation in the soil, to aid in the work of pulverisation usually brought about by hand labour, *i.e.*, tillage.

It is no longer used in this sense, but is now the name given to any material which is intended, by its application to the soil, to restore those constituents which have been removed by cropping and thus to render it possible for the soil to supply another crop with a sufficiency of plant food.

The constituents of a soil which are most liable to be deficient in amount, and which it is therefore advisable to replenish by manuring, are combined nitrogen, phosphates, and potash compounds.

Manures, therefore, are usually valued according to their richness in these three constituents, though in the case of many so-called natural manures, *e.g.*, farm-yard manure, many other constituents which may serve as useful items of plant food are also present.

These natural manures, from a chemical standpoint, are exceedingly complex, and might, perhaps, with propriety have been left until the simpler chemical manures had been discussed; but, on account of their extensive use and their great importance in farming practice, they will be described first.

Farm-yard Manure.—This has long been the most popular manure used on the farm. It would seem that, inasmuch as it contains the remains of the vegetable substances used as food and litter on the farm, it should be a most suitable means of restoring to the land the ingredients removed from it in the crops. A little thought, however, will show that it cannot restore completely such losses. Some of the crops are sold;

often these are particularly rich in nitrogen, potash, and phosphates, and of those eaten by the animals of the farm only a portion is voided as excrement—the animal has to build up its body out of the materials supplied in its food. This consumes large quantities of nitrogen and phosphates particularly. Then, too, the production and sale of milk removes large quantities of manurial ingredients from the soil, and though butter contains little other than carbonaceous material, cheese is highly nitrogenous.

It will be advisable to briefly consider the chemical nature of the raw materials which go to form the average farm-yard manure. The ingredients of this substance may be first divided into two groups:—

I.—Animal excrements, both solid and liquid.
II.—Litter and waste food materials.

The *excreta of animals* consist of the undigested parts of the food consumed by them, together with excretions consisting of effete matters resulting from waste of their tissue and the water drunk by them which they have not exhaled as vapour from their lungs or skin.

The chemical nature and the total quantity of the excreta depend very largely upon the character and quantity of the food supplied. This is especially true of the solid portion, which consists mainly of the undigested matter of the food, but contains also certain products derived from the digestive fluids, *e.g.*, the bile, pancreatic juice, &c.

The liquid portion of the excreta, on the other hand, consists mainly of water, holding in solution substances produced by the wear and tear of the muscles, &c., of the animal, these waste products being separated from the blood stream of the animal by appropriate organs. Of course these matters originally came from the food, but they are not the immediate products, as are most of the constituents of the solid excreta.

Both the liquid and solid portions of the excreta contain large quantities of substances of little or no value as fertilisers directly; but, inasmuch as they readily undergo putrefactive changes resulting in the liberation of carbon dioxide and other gases and the production of bulky carbonaceous substances akin to humus in their nature, these ingredients are of considerable importance in determining the effect of farm-yard manure on land.

The chemical character of the excreta produced on the farm depends upon a number of conditions—the food, the breed of animals kept, their age, whether fattening, working, or milking, and other circumstances.

Obviously, if an animal is growing in size, or is yielding milk, its food must contain much more of the important flesh-forming constituents than its excreta; while in the case of an animal not increasing in size nor providing milk, one might expect that the excreta would contain practically all the matters taken in its food, with the exception of those consumed in respiration. Remembering these facts, it is not surprising to find among published analyses of the excrements of animals considerable discrepancies.

The following table gives the percentage amounts of the most important manurial constituents of the excrements of the common animals*:—

	Water.	Nitrogen.	Potash.	Phosphoric acid.
Cattle dung ...	—	·20	·10	·17
,, urine ...	—	·58	·49	—
Horse dung ...	—	·44	·35	·17
,, urine ...	—	1·55	1·50	—
Sheep dung ...	—	·55	·15	·31
,, urine ...	—	1·95	2·26	·01
Pig dung ...	—	·60	·13	·41
,, urine ...	—	·43	·83	·07
Hen manure (fresh)	60·0	1·10	·56	·85
Pigeon manure (dry)	10·0	3·20	1·00	1·90
Human excrement...	77·2	1·00	·25	1·09
,, urine ...	95·9	·60	·20	·17

The table on the opposite page gives analyses of the excrements of the common farm animals and of man. The figures are quoted by Storer† from analyses by Stoeckhardt and Way:—

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* U.S. Dept. of Agriculture, Bulletin 15, 1893.

† "Agriculture in Some of its Relations to Chemistry," Vol. I., p. 489.

PERCENTAGE COMPOSITION OF ANIMAL EXCREMENT.

	SOLID EXCREMENT.					LIQUID EXCREMENT.				
	Sheep.	Pigs.	Horses.	Cows.	Men.	Sheep.	Pigs.	Horses.	Cows.	Men.
Water	58	80	76	84	75	86·5	97·5	89·0	92·0	97·0
Solid matter	42	20	24	16	25	13·5	2·5	11·0	8·0	3·0
Ash	6	3	3	2·4	2·9	3·6	1·0	3·0	2·0	1·0
Organic matter	36	17	21	13·6	22·1	9·9	1·5	8·0	6·0	2·0
Nitrogen	·75	·6	·5	·3	1·5	1·4	·3	1·2	·8	·6
Phosphorus pentoxide	·6	·45	·35	·25	1·1	·05	·12	—	—	·05
Alkalies	·3	·5	·3	·1	·4	2·0	·2	1·5	1·4	·15
Lime and magnesia	1·5	·3	·3	·4	·8	·6	·05	·8	·15	·03
Sulphur trioxide	·15	·05	·05	·05	·05	·4	·05	·15	·15	·01
Common salt	·025	·05	trace	·005	·05	·25	·5	·2	·1	·6
Silica	3·2	1·6	2·0	1·6	·4	trace	trace	·025	·01	—
Ferric oxide	—	—	—	—	·13					

From the preceding tables it will be seen that the excrements of the sheep are less watery than those of the other animals, while the solid excrement of the cow and the urine of pigs are richest in water.

A large proportion of the solid matter in all cases consists of substances comparatively useless as plant food—carbonaceous matter, lime and magnesia, silica, &c. Other analyses of the excrements of horses and cows have been published by Boussingault and by Audoynaud and Zacharewicz.[*] The results expressed in percentages were as follows:—

	Boussingault.			Audoynaud and Zacharewicz.		
	Nitrogen.	Potash.	Phosphorus pentoxide.	Nitrogen.	Potash.	Phosphorus pentoxide.
Cow urine ...	1·12	1·39	—	·97	1·32	trace
,, dung ...	·44	·04	·14	·42	trace	·10
Horse urine ...	1·56	1·06	trace	1·48	·80	trace
,, dung ...	·57	·15	·40	·55	trace	·30

In the paper referred to the authors estimate the annual yield per cow at 31·5 kilograms of nitrogen and 40·8 kilograms of potash in the urine and 42 kilograms of nitrogen, 4·2 of potash, and 12 of phosphorus pentoxide in the dung; while in the total excreta of one horse per annum will be 37·8 kilograms of nitrogen, 13·1 of potash, and 14·4 of phosphorus pentoxide.

They think that the potash in dung is that existing in the food as inorganic salts, while that in the urine existed in the food in combination with organic acids. They found a deficiency of potash in the excreta even after allowance for that removed in the milk of the cows and the growth of the bodies of the animals. They account for this by attributing it to loss through the skin. The dust removed from the skin by curry-comb and brush contained from 2 to 2·2 per cent. of potash in the case of cows and from 7·4 to 9·7 per cent. in that of the horses.[†] A much larger amount of potash is exuded from the skin of the sheep.

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[*] *v.* Abst. in Jour. Soc. Chem. Ind. 1886, 541.

[†] An analysis of the perspiration of a horse was published by Smith (Journal of Physiology 11, 497; also Jour. Chem. Soc., 1891, abst. 349):—

Water	94·3776 %	
Organic matter .	0·5288	(chiefly albuminoids)
Ash	5·0936	

The ash contained	Chlorine .	0·3300
	Lime ..	0·0940
	Magnesia	0·2195
	Soda ..	0·8265
	Potash ..	1·2135

The composition of the excreta of animals is liable to such enormous variations in composition, according to the nature of the food and other conditions, that it is almost impossible to give any average figures.

As showing how variable the utilisation of the ingredients of food may be in the case of animals living under different conditions, the following table may be quoted from Warington* as giving the destination of the nitrogen supplied in the food. For every 100lb. of nitrogen consumed :—

	Obtained as carcass or milk.	Voided as dung.	Voided as urine.	In total excrement.
Horse at rest ...	none	43·0	57·0	100
,, work ...	none	29·4	70·6	100
Fattening oxen ...	3·9	22·6	73·5	96·1
,, sheep ...	4·3	16·7	79·0	95·7
,, pigs ...	14·7	25·0	60·3	85·3
Milking cow ...	24·5	18·1	57·4	75·5
Calf fed on milk ...	69·3	5·1	25·6	30·7

As has already been stated, the dung consists mainly of the undigested portion of the food mixed with a certain amount of the residue from the bile and other digestive fluids. It is therefore to be expected that the amount of plant food, say nitrogen, in the solid excrement will be greater the less digestible the food consumed.

The litter and waste food.—Litter serves several useful purposes. Besides the obvious advantages attending its use from the point of view of cleanliness and comfort for the animal, it also fulfils several other functions. It greatly increases the bulk of the manure, rendering it more porous and therefore better able to retain the valuable liquid portion of the excreta, it provides a large amount of carbonaceous matter which will eventually be converted into humus, and it adds its quota of plant food, small though it be. It has a considerable effect upon the various fermentative changes which the excreta of animals so readily undergo, both by its influence on the porosity and consequent admission of air and also by the micro-organisms with which it is said to be often abundantly supplied.

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* "Chemistry of the Farm."

Various substances are used as litter in different districts. The following are the chief:—

1. Straw.
2. Peat or peat moss.
3. Dried bracken.
4. Dried leaves.
5. Sawdust.
6. Tanners' refuse.

Straw is the material most largely used as litter on the farm. Its composition varies considerably, but it always consists mainly of woody fibre, cellulose, &c., which have practically no manurial value; its nitrogen, phosphoric acid, and potash are always small in quantity. The average proportion of manurial constituents in the straw of different plants is seen in the following table:—

	% Nitrogen.	% Potash.	% Phosphoric acid.	% Lime.
Wheat ...	·48	·9	·25	·31
Barley ...	·57	1·2	·26	·39
Oats ...	·72	1·2	·19	·41
Rye ...	·57	1·4	·28	·45

A point which is attracting great attention just now is the general occurrence of denitrifying organisms on the outsides of the stems of wheat and other straws (see Chap. IV.).

Mingled with the litter there are generally considerable quantities of the wasted fodder supplied to the cattle or horses, consisting often of hay or straw. The manurial value of such material is similar to that of the straw used as litter.

Peat, or better, peat moss, is largely used as litter in Germany, &c., and to some extent in town stables in England. It possesses great porosity and absorptive powers for liquids and in itself often contains a considerable quantity of nitrogenous matters, varying in different samples from ·3 to as high as 2·0%. It also has strong absorptive powers for gases, *e.g.*, ammonia, and acts as an antiseptic in preventing the too rapid putrefaction of the organic matter of the excreta and the injury to the health of the animals resulting from such putrefaction. The manure produced is richer, especially in nitrogen, than that produced by straw.

The chief constituents of peat, according to American analyses,* are as follows:—

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* U.S. Dept. of Agric., Bulletin 15, 1893.

Water	61·50 %
Nitrogen	·85
Potash	·18
Phosphorus pentoxide ...	·08

Dyer found in

	Peat moss.	Wheat straw.
Water	12·46 %	10·33 %
Nitrogen	·81	·62
Lime	·15	·29
Potash	·01	·99
Phosphorus pentoxide ...	·02	·11
Silica	·72	5·74
Magnesia, &c.	·48	·47

Or, according to an analysis quoted by Ivison Macadam,* dried peat litter contains—

Moisture ...	9·12	
Organic matter ...	89·39	containing 0·51 % nitrogen
Alkaline salts ...	·03	
Phosphates ...	·16	
Calcium carbonate	·98	
Silica	·32	
	100·00	

Analyses of fibres extracted from peat obtained in Würtemburg and Silesia and of moss litter from North Germany were made by Fleischer in 1883† :—

	Würtemburg fibre.	Silesian fibre.	German peat moss.
Nitrogen	2·20 %	2·90 %	·90 %
Phosphorus pentoxide	·06 %	·06 %	·04 %
Lime	1·72 %	3·10 %	·20 %

Peat sometimes contains iron pyrites, and in some cases arsenic is present in the pyrites. The manure made with such peat may be destructive to plant life.

Dried bracken is often used as litter in mountainous and thickly wooded districts, *e.g.*, in the English Lake district and the New Forest, in Scotland and Ireland, and in certain parts of Germany.

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* Jour. Soc. Chem. Ind. 1888, 80.

† Jour. Chem. Soc. 1884, absts. 105.

It is not so absorbent as other litters, but is of value on account of its composition. This varies with the age at which it is cut and other circumstances. A dried sample examined by Homberger* contained ·706 % nitrogen, ·13 % potash, and ·12 % phosphorus pentoxide, while two samples examined by J. Hughes contained in one case (young plants) 2·42 % nitrogen, 1·15 % potash, and 0·6 % phosphorus pentoxide, while in the other (old plants) there were only 0·90 % nitrogen, 0·10 potash, and 0·30 of phosphorus pentoxide.

Dried leaves.—These are only rarely used and are not of much value. According to numbers obtained from American investigations† autumn leaves contain about

·75 % nitrogen,
·10 to ·50 % potash,
·06 to ·30 % phosphorus pentoxide.

Sawdust is used in stables in large towns. It has good absorptive powers, and according to Storer (just quoted) contains about

1·0 % nitrogen,
·10 % potash,
·05 % phosphorus pentoxide.

It renders horse manure very open and porous and therefore favours rapid oxidation and fermentation, sometimes to a harmful extent. It would be less objectionable as a litter for cows. The turpentine found in pitch-pine sawdust may seriously retard its decomposition in the soil.

Tanners' refuse.—This is sometimes used as a litter, but is of comparatively little value. Storer gives as its average composition:—

Nitrogen	·16 %
Potash	·08 %
Phosphorus pentoxide ...	·04 %

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* Jour. Chem. Soc. 1886, abst. 485.
† Quoted by Storer, Agriculture, &c., Vol. I., p. 446.

Farm-yard manure consists usually of the mixed excrements of the animals of the farm, together with the litter used for their bedding. To it are added any waste organic matters occurring near the farmstead, including animal offal of various kinds, vegetable refuse, and too often the waste matter from the thrashing machine, often containing the seeds of weeds.

According to German authorities the average amount of manure yielded per day per head by the various animals of the farm may be taken as the following:—

	Total excrement.	Straw required.	Nitrogen in whole.
The horse ...	28lb.	5lb.	·19lb.
,, cow ...	73lb.	8lb.	·28lb.
,, pig ...	8·3lb.	4lb.	·07lb.
,, sheep ...	3·8lb.	·6lb.	·04lb.

American estimates are much higher[*]:—

Animal.	Food.	Manure per day.	Composition of manure. Nitrogen	Potash.	Phosphorus pentoxide.
Cows ...	Hay, silage, bran, cotton-seed meal, &c.	81·5lb.	·50%	·29%	·45%
Horses†	Hay and oats	52·5 ,,	·47%	·94%	·39%
Sheep ...	Grain, beets, & hay	7·2 ,,	1·00%	1·21%	·08%
Pigs ...	Maize meal	3·5 ,,	·83%	·61%	·04%

The composition of the manure produced on a farm must vary considerably owing to a great number of varying conditions. It is obvious, therefore, that any particular analysis is of little value as a means of judging of the nature of manure produced in other cases. Large numbers of analyses have been published, some showing in great detail the substances present. An often quoted series of analyses of farm-yard manure was made by Voelcker many years ago.

A summary of his results, as quoted by Storer,‡ is here given:—

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[*] Bulletin 27 of the New York Cornell Station.

† The horses were working. The quantities are estimated on the assumption that three-fifths of the manure was collected.

‡ Agriculture, &c., Vol. I., p. 521.

	Fresh manure 14 days old.	From heap 3½ months old.	Well rotted, 6 months old.
Water	66·17 %	69·83 %	75·42 %
Soluble organic matter ...	2·48	3·86	3·71
,, inorganic ,, ...	1·54	2·97	1·47
Nitrogen, total	·64	·74	·61
Phosphorus pentoxide, total	·32	·32	·45
Potash	·67	1·22	·49
Lime	1·19	1·34	1·78
Magnesia	·15	·05	·14
Ammonia	·12	·08	·13
Nitrates	none	traces	none

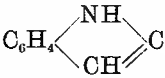
Fermentation of Farm-yard Manure.—Fresh manure soon begins to ferment and to change its character. This is due to the effect of the micro-organisms which find a suitable breeding ground in the complex organic substances present in the manure. An account of the bacteria of stable manure and their action was given in a paper by Herzfeld in the "Centralblatt für Bacteriologie" in 1895, and a translation appeared in the Journal of the Society of Chemical Industry for 1895, p. 449.

According to this paper the fermentations which manure undergoes, partly in the stables, &c., but mainly in the heap and finally on the land, may be divided into—

(a) Fermentations of the fatty acids.
(b) Fermentations of the amido-compounds.
(c) Putrefaction fermentation.
(d) Ammoniacal or urea fermentation.
(e) Sulphuretted hydrogen fermentation.
(f) Cellulose or methane fermentation.
(g) Fermentations of the carbo-hydrates.

(a) Many of the fatty acids, or rather their salts (best the calcium salts), are capable of undergoing changes under the action of various bacilli, micrococci, and other bacteria, generally giving rise to the formation of other simpler organic acids, often carbon dioxide and sometimes hydrogen and alcohol.

(b) Amido-acids and other amido-compounds, *i.e.*, compounds containing (NH_2) are formed by the putrefaction of albumen. Tyrosine, $OH.C_6H_4.CH_2.CH(NH_2).COOH$, *para-oxyphenyl a-amido-propionic acid*, leucine—$CH_3.(CH_2)_3.CH(NH_2).COOH$, *a-amido-caproic acid*, asparagine—$COOH.CH_2.CH(NH_2).CONH_2$, *amido-succinamic acid*, and glycocol, $CH_2.(NH_2).COOH$, *amido-acetic acid* are among such products.

Tyrosine is converted by fermentation, if air be excluded, into *indol*,  $C_6H_4\left\langle\begin{matrix}NH\\ \\ CH\end{matrix}\right\rangle CH$, carbon dioxide, and hydrogen; in the presence of air other substances, like phenol, C_6H_5OH, are formed and the nitrogen is converted into ammonia. *Leucine* by its fermentation forms valerianic acid, $C_4H_9.COOH$, ammonia, carbon dioxide, and hydrogen.

(c) Putrefactive fermentation is the rapid decomposition of albuminoid substances attended by the evolution of evil-smelling gases and produced by the agency of various species of bacteria. Generally the first step is the conversion of the insoluble or colloidal albuminoids into soluble and diffusible peptones; these next split up, yielding amido-acids, *e.g.*, leucine, &c. These in turn are decomposed into fatty acids and ammonia and the fatty acids then ferment as described under (a).

However, the kind of change produced is determined to a great extent by the admission or exclusion of air from the fermenting substances. Indeed, the presence or absence of air from the decomposing mass determines the species of bacteria which can flourish in it. Bacteria are sometimes classed into two great groups:—

Aerobic bacteria, which require the presence of oxygen, and

Anaerobic bacteria, which only perform their functions in the absence of oxygen.

The distinction is not altogether satisfactory, as under conditions of air exclusion certain aerobic organisms can carry on their work if nitrates be present. In the case of the aerobic bacteria the compounds formed by their vital processes are usually of a simple character, *e.g.*, water, carbon dioxide, and ammonia. Such fermentation is sometimes called mouldering or decay and is not attended by the evolution of foul-smelling gases.

The anaerobic organisms, on the other hand, tend to produce unoxidised products, some of which are highly complex, and the gases evolved consist of methane, CH_4, hydrogen, sulphuretted hydrogen, &c., &c. Many of these products are possessed of disagreeable smells and the changes leading to their production are considered as true putrefaction. These putrefactive changes can be brought about by a great number of different organisms and the albuminoid substances are the chief raw material for their activity. Many of the bad-smelling gases evolved have not been identified. Among other products, amines, *e.g.*, trimethylamine, $N(CH_3)_3$, volatile acids, *e.g.*, butyric acid, $C_3H_7.COOH$, and caproic acid, $C_5H_{11}.COOH$, and mercaptans, *e.g.*, $C_2H_5.SH$, have been detected.

In a manure heap both aerobic and anaerobic organisms perform their functions, the former chiefly at first and until the air in the interstices of the manure has been exhausted, producing mainly carbon dioxide, water, and ammonia. Then the anaerobic bacteria begin to operate and evil-smelling gases come off. The evolution of heat, which is aften considerable during the life of the aerobic organisms, diminishes.

(d) Ammoniacal or urea fermentation. This has already been briefly referred to (*v.* p. 65). The main reaction is there given as—

$$CO(NH_2)_2 + 2H_2O = (NH_4)_2CO_3,$$

thus giving ammonium carbonate; in addition a reaction expressed by the following equation :—

$$\underset{\text{Urea.}}{CO(NH_2)_2} + H_2O = \underset{\text{Ammonium carbamate.}}{NH_4.O.CO.NH_2}$$

—resulting in the formation of ammonium carbamate, has been detected. At least five or six different bacteria, some micrococci, some bacilli, and even some moulds have been shown to have the power of bringing about this change.

(e) Sulphuretted hydrogen fermentation. A large number of different bacteria have been shown to have the power, under certain conditions which are not exactly known, of producing sulphuretted hydrogen by their action upon albumen.

(f) Cellulose fermentation. Cellulose, which forms the larger portion of the tissues of straw and other vegetable matter, is, under the influences of an organism known as *Bacillus amylobacter* and other bacteria, converted eventually into carbon dioxide, CO_2, and methane, CH_4, though many intermediate products, *e.g.*, acetic acid, $CH_3.COOH$, free hydrogen, and perhaps butyric acid, $C_3H_7.COOH$, have been detected.

The process is anaerobic and the bacteria producing it have been detected in the intestines of cattle.

(g) Other carbohydrates, chiefly starch, various sugars, and gums, occur in dung and readily undergo change by the influence of many bacteria, some aerobic, some anaerobic.

Carbon dioxide, water, lactic acid, $CH_3.CH.OH.COOH$, butyric acid, $CH_3.CH_2.CH_2.COOH$, and sometimes free hydrogen are formed.

A study of the gases evolved during fermentation of manure was made by Schloesing in 1892.* He found that in presence of air the temperature of a manure heap is raised by the action of aerobic organisms until purely chemical oxidation sets in and may go on until the temperature is so high that destruction of the organisms is effected. No combustible gases are produced. By allowing the fermentation to proceed in a current of nitrogen or other indifferent gas the anaerobic bacteria only are active and carbon dioxide and marsh gas are chiefly produced.

The details of one experiment may be of interest. 124·4 grammes of fresh manure were allowed to ferment in an atmosphere of carbon dioxide for two months; in this period nearly 9 litres of gas were evolved, the maximum rate of evolution being 16·3 c.c. per hour (on the sixth day). The gas contained 15·8 c.c. of hydrogen, 4217·5 c.c. of carbon dioxide, and 4577·4 c.c. of marsh gas (equal to 4·72 grammes of carbon, 6·033 grammes of oxygen and 0·819 gramme of hydrogen).

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* "Annales Agronomiques," 18, 5; J.C.S., 1892, abst. 1123.

The loss suffered by the manure is shown by the following table, which gives the amounts, in grammes, of the various constituents in the dried manure before and after the experiment:—

	Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Minerals.
Before ...	12·67	1·653	10·70	0·453	3·69
After ...	7·92	1·125	7·08	0·392	3·79
Loss ...	4·75	0·528	3·70	0·061	—0·10 (gain)

No free nitrogen was found in the gases, the loss of nitrogen being due to its liberation as ammonia, which would be lost in drying. The oxygen and hydrogen in the gases evolved, including the hydrogen lost as ammonia, exceed by 2·333 grammes and 0·305 gramme that lost by the manure, showing that water enters into the reactions by which these gases are produced.

Preservation of Farm-yard Manure.—The best means of using farm-yard manure, whether fresh or rotted, and the most advantageous manner of treating it so as to minimise the loss of fertilising ingredients, are matters which have received much consideration and about which the greatest diversity of opinion, especially among farmers, exists.

Such obvious precautions as the prevention of loss of soluble matter by drainage hardly need mention here, unless it be to show how rich in fertilising materials such drainage often is. In fresh manure the liquid portion consists mainly of urine, which has been shown to be rich in nitrogen and potash.

The dark brown drainage from old manure heaps is often rich in manurial matters; a sample analysed by Voelcker contained nearly 2% of solid matter, including 0·04% nitrogen, 0·52% of carbonate and chloride of potassium, and a considerable quantity of phosphoric acid. It is obviously desirable that such drainings should be preserved, either by the use of sufficient litter—best peat or peat moss—to absorb it, or by collecting it in a tank.

Of more importance from the chemical aspect is the loss of nitrogen and other substances which occur during fermentation. A great amount of attention has lately been directed to this matter, more especially with reference to the methods of minimising the loss. The loss of nitrogen occurs chiefly in two ways, by volatilisation of ammonia from ammonium carbonate and by the formation of free nitrogen.

According to Berthelot and André, ammonium carbonate dissociates when it volatilises, yielding ammonia, carbon dioxide, and water:—

$$(NH_4)_2CO_3 \rightleftarrows 2NH_3+CO_2+H_2O.^*$$

In accordance with the law of dissociation the equilibrium represented above is attained when the product of the square of the number of molecules of ammonia into the number of molecules of carbon dioxide present in unit volume reaches a certain value. Now this product may be reached by an increase of both or of only one of the two factors; if either be increased the other factor will diminish if the product is to remain the same. It is obvious, therefore, if the amount of carbon dioxide in the surrounding air be increased, the amount of ammonia set free by dissociation will be diminished. Hence, if the production of carbon dioxide by the fermentation of merely carbonaceous matters in a manure heap can be encouraged, the dissociation of ammonium carbonate will be diminished and the loss of ammonia hindered.† Another important consideration affecting this source of loss of nitrogen as ammonia is the renewal of the gas in the interstices of the manure by diffusion. If the gaseous carbon dioxide and ammonia are removed by, say, a current of air, the dissociation of the ammonium carbonate will proceed more rapidly.

A method of preventing, or rather of lessening, the loss of ammonia from manure heaps which has been recommended and used for many years is the strewing of powdered gypsum ($CaSO_4.2H_2O$) over the heap or in the stall. This was supposed to act by producing calcium carbonate and ammonium sulphate. This reaction could, even in solution, only go on to a limited extent, in accordance with the mass-action law (see p. 86), and according to many recent experiments gypsum is quite useless as a preservative.* These investigators found that kainite and superphosphate or free phosphoric acid are very effective in preventing loss of ammonia.

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* See Appendix to Chap. IV.

† Dehérain recommends (Compt. Rend 1898, 1305) that the soiled litter be removed to the manure heap as often as possible and the stable or cow-shed gutters be rinsed with water to carry the liquid excreta into the liquid-manure tank and that the dung heap be well heaped up and watered with the liquid from the tank. In this way a constant production of carbon dioxide by fermentation is produced and loss of ammonia hindered.

As the result of a series of experiments Kreuz and Gerlach† arrived at the following conclusions. Conversion of urea into ammonium carbonate takes place rapidly either in the presence or absence of air and without any liberation of free nitrogen. The ammonium carbonate dissociates if the dung dries and is easily volatile except in an atmosphere of carbon dioxide; the loss is greater if a stream of air pass through the dung. The nitrogen of the ammonium carbonate which remains in the dung is gradually, in presence of air, converted into nitric acid, again with no liberation of free nitrogen. The nitric acid so formed, however, is, by the denitrifying bacteria, decomposed with evolution of free nitrogen. This decomposition proceeds either in presence or absence of air, provided the bacteria are furnished with suitable food materials, such as straw, grape sugar, glycerin, sodium lactate or citrate, the green parts of plants, &c. The whole of the nitrogen of the nitrates decomposed is not evolved as free nitrogen, but about 10% of it is converted into highly complex organic substances resembling albumen.

The loss of nitrogen which animal refuse undergoes during storage, results from the liberation of ammonia and of free nitrogen. If the manure be kept in a loose, porous condition, the volatilisation of ammonia is favoured; if compact, so as to exclude air, much free nitrogen escapes, but the ammonia formed is retained. The loss of nitrogen, which is mainly suffered by the liquid portion of the manure, is shared to a small extent by the solid dung and the straw, the nitrogenous compounds of which, by the action of the bacteria, are converted into amido-compounds, which suffer the same fate as the urea. If the manure has to be kept long it is desirable to cover the heap with soil, preferably with peaty soil.

Maercker and Schneidewind‡ found that in a deep stall the loss of nitrogen from dung, analysed immediately after the fattening animals were removed, was small, amounting to about 13·25 % of the original amount, and was about the same in summer as in winter. If, however, the manure was left for four weeks in the stall after the animals had been removed, the loss in warm weather amounted to 34·8 % of the whole. In open dung heaps the loss of nitrogen observed was 37·4 % of the total, while in a parallel experiment in a covered heap 36·9 % of the total nitrogen was lost; but the covered heap held manure containing 70 % of water, while the open one contained 78 %. The large loss of nitrogen from the covered heap is due to the higher temperature and drier state of the dung, favouring the volatilisation of ammonia. An addition of 30 % of marl to the manure reduced the loss of nitrogen from 22·6 %, to 9·9 %, and a mixture of 30 % marl and 2 % of turf litter reduced it to 6·1 %. The best result was obtained by the addition of 6 % of sodium hydrogen sulphate, $NaHSO_4$ (containing 1·5 % of free acid), when the loss was diminished to 1·3 % of the nitrogen originally present.

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* Burri, Herfeldt, and Stutzer, Journ. Landwirt. 1895, 1.

† Jahresbericht Agricultur-Chemie 1899, p. 98.

‡ Jahr. Agric. Chem. 1899, 100.

The action of free sulphuric acid in preventing loss of nitrogen is partly attributable to its combining with the ammonia and partly to its preventing the growth of denitrifying bacteria.

The application of fresh manure to the soil probably leads to a greater conservation of its nitrogen, but there is considerable risk of excessive denitrification being set up in the soil, both by the large amount of oxidisable carbonaceous matter and the numerous denitrifying organisms which are present in straw and the fæces of most animals, and this denitrification may extend to the nitrates already present or being produced in the soil. Well-rotted manure, on the other hand, though it may have lost some of its nitrogen, will be much less likely to bring about denitrification. It would seem, therefore, best to favour the fermentations which destroy carbonaceous matter, while attempting to retain by absorption in peat moss or other porous material the ammonia which volatilises. In this way the denitrifying organisms will be quickly deprived of their favourable environment, and their destructive effects, both in the manure heap and subsequently in the soil, will be weakened.

The addition of kainite, or better, of acid substances, *e.g.*, free sulphuric acid or superphosphate, has been highly recommended as a means of preserving nitrogen. Heiden* states that by strewing the stalls in which cattle are kept three times a day with superphosphate at the rate of 2lb. for every 1000lb. live weight a great economy is effected in the manure, and this is true whether the stalls are cleaned out frequently or the dung and litter be left under the cattle for six weeks.

From extensive experiments made by Holdefleiss†, the effect of covering the manure with earth was shown to greatly preserve the nitrogen, while allowing of the fermentation and consequent loss of the carbonaceous matter; superphosphate and kainite, which also prevent loss of nitrogen, when applied at the rate of about 2% of the manure, interfere with other fermentative changes and allow the straw to remain practically intact. Hence they act as antiseptics rather than absorbents.

Other Organic Manures.—A number of other refuse matters of vegetable or more frequently animal origin are used as manures, the chief being—

Guano.
Pigeon and fowl dung.
Fish refuse or fish guano.
Sea-weed.
Dried blood.
Meat meal or meat guano.
Bones.
Woollen refuse, shoddy manure.
Soot.
Oil-cakes, and oil-seed refuse.

These can only be briefly dealt with here.

Guano is the dried dung of sea birds, together with portions of their feathers, bones, and the refuse of their food; the older deposits also contain the remains of seals, walruses, &c. Guano accumulates on islands or near the coasts in tropical climates, the chief deposits being found in North and South

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* Bieder. Centr. 17, 154; J. Soc. Chem. Ind. 1888, 332.
† Jahresbericht über Agricultur-Chemie 1900, 117.

America, Africa, Australia, the West Indies, and islands in the Pacific. The original Peruvian guano, the deposits of which are now exhausted, was a very valuable and concentrated manure, containing nearly half its weight of ammonium salts—urate, $C_5H_3(NH_4)N_4O_3$, oxalate, $(NH_4)_2C_2O_4$, and phosphate, $(NH_4)_3PO_4$, together with calcium-phosphate and potash compounds.

It contained from 11 to 16% of nitrogen and from 10 to 12% of phosphorus pentoxide.

The guano now obtainable contains much less nitrogen (about half or a little more), though often much more phosphates.

Two varieties of guano are now imported :—

(1) Nitrogenous and phosphatic. These have accumulated in practically rainless districts and the excreta which formed them have been desiccated before much fermentation was possible. True Peruvian guano from the Chincha Islands, and Ichaboe guano, a recent deposit, are examples of such guanos, the latter usually containing from 7 to 11% nitrogen and 5 to 15% phosphorus pentoxide.

(2) Phosphatic. These are the remains left after the weathering by rain, &c., of the dung of sea birds. Owing to the moist state in which it has been kept the nitrogenous matter has been lost, by solution or volatilisation, and only the mineral (phosphatic) portion left.

Considerable deposits of guano were discovered about four years ago on islands lying off Damaraland, on the West Coast of Africa, and are being extensively worked.

An analysis of Damaraland guano gave the following numbers* :—

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* Barth, Jahresbericht über Agric.-Chem. 1900, 118.

Moisture		19·00 %
Organic and volatile matters		33·94 %
Including Total nitrogen	7·72 %	
Ammoniacal nitrogen	3·26	
Organic nitrogen	4·00	
Nitric nitrogen	0·46	
Ash		47·06 %
Including Total phosphorus pentoxide	11·22 %	
Soluble ,, ,,	3·87	
Potash	2·44	
Sulphur trioxide	5·06	
		100·00

In some samples the phosphorus pentoxide and potash are higher in quantity.

As types of the less valuable products, Baker Island, Mexillones, and Lacepede guanos may be quoted. In these the nitrogen varies from 0·5 to 2·0 %, while the phosphorus pentoxide may reach as high as 34 % and is usually above 23 %.

The nitrogenous guanos are particularly valuable from the fact that a large portion of their phosphates are soluble and the nitrogen which they contain is in a readily available form, being present as ammonium salts or in such easily decomposable substances as *uric acid*, $C_5H_4N_4O_3$, or *guanine*, $C_5H_5N_5O$, a body first obtained from guano.

Uric acid and guanine are interesting from their close relationships to xanthine, $C_5H_4N_4O_2$, found in meat extracts; to theobromine, $C_7H_8N_4O_2$ (dimethyl xanthine), the characteristic ingredient in cocoa; and to caffeine or theine, $C_8H_{10}N_4O_2$ (trimethyl xanthine), the main valuable constituent of coffee and tea (*v.* Chap. XI.).

In the phosphatic guanos the phosphoric acid is mainly present as tricalcium phosphate, and therefore not easily available to plants. Such guanos are often used for conversion into superphosphate.

The chemical nature of guano is highly complex, as is indicated by what has already been said. It is almost impossible to say how the various acids and bases present in such a mixture are distributed, but attempts to do so have been made.

Wagner* gives the following as the composition of three samples of Peruvian guano:—

	I.	II.	III.
Ammonium chloride	2·25	6·50	4·2
,, urate	12·20	3·24	9·0
,, oxalate	17·73	13·35	10·6
,, phosphate	6·90	6·25	6·0
,, carbonate	0·80	—	—
,, bromate	1·06	—	—
,, magnesium phosphate	11·63	4·20	2·6
Sodium phosphate	—	5·29	—
,, chloride	0·40	0·10	—
,, sulphate	4·92	1·12	3·8
Potassium sulphate	4·00	4·23	5·5
Calcium phosphate	20·16	9·94	14·3
,, oxalate	1·30	16·36	7·0
,, carbonate	1·65	—	—
Sand and clay	1·68	5·90	4·7
Water and organic matter ...	13·32	23·32	32·3
	100·00	99·80	100·0

Pigeon and fowl dung.—These substances, according to Storer,† were formerly much prized as manures, and played an important part in Roman, Persian, and Egyptian husbandry. In France, too, large dovecotes formerly constituted an almost necessary adjunct to farmsteads. Their importance has diminished since the introduction of nitrate of soda, kainite, and other artificial manures.

Storer gives as the percentage composition of the fresh excreta of the common domestic birds—

	Fowls.	Pigeons.	Ducks.	Geese.
Water	56·0	52·0	56·6	77·1
Organic matter ...	25·5	31·0	26·2	13·4
Nitrogen	1·6	1·8	1·0	0·6
Phosphorus pentoxide	1·7	1·7	1·4	0·5
Potash	0·8	1·1	0·6	1·0
Lime	2·2	1·7	1·7	0·8
Magnesia	0·8	0·5	0·4	0·2

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* Chemical Technology 1892, p. 424.

† "Agriculture," Vol. I., 368.

He gives as an estimate of the quantities produced by each bird per year—pigeon, 6lb.; hen, 12lb.; duck, 18lb.; goose or turkey, 25lb.

Ulrich* gives the following as the average percentage composition of the dung of poultry:—

	Pigeons.	Fowls.	Ducks.	Geese.
Water	62	65	53	82
Organic matter ...	31—32	21—26	40	14
Nitrogen	1·2—2·4	0·7—1·9	0·8	0·6
Phosphorus pentoxide...	3·0—4·2	5·0	3·5	0·9
Alkaline salts ...	2·0—2·2	1·2—1·6	0·4	3·1
Ash	6—7	9—14	7	4

He estimates the annual production at—

Pigeons ...	2·5 kilos	or 5·6lb.	per head
Fowls ...	5·5 ,,	or 12·4lb.	,,
Ducks ...	8·5 ,,	or 19·1lb.	,,
Geese ...	11·0 ,,	or 24·8lb.	,,

and recommends that the manure be mixed with water containing sulphuric acid (30lb. of acid to 1cwt. of manure), in order to prevent loss by volatilisation of ammonia.

Deposits of the dung of sea birds occur at places on the coast, sometimes in sufficient quantities to be important. The material is rich in nitrogen and phosphoric acid, though in ordinary climates somewhat too heavily charged with water to be very valuable except locally. A deposit of this character from the coast of Ireland, examined by the author, contained, in the damp sample, 47·5% water, 1·25% nitrogen, and 8·5% phosphoric acid.

Bats' guano.—Deposits of this substance are found in caves in tropical climates, occasionally in sufficient quantities to be useful as manure. Its composition varies considerably. A sample from Eboli, Salerno, analysed by Paris†, contained—

Water	18·02 %
Nitrogen	3·00 ,,
Ash	52·87 ,,

The ash contained in each 100 parts 2 of potash, 13·8 of lime,

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[*] Bieder. Centr. 1900, 3; Jour. Chem. Soc. 1900, abst. ii., 308.

[†] Annales Agronomiques, 1897, 47.

20·7 of phosphorus pentoxide, and a small quantity of copper. The nitrogen was almost all as nitrates. An American analysis* gives as the composition of bats' guano—

Water	40·0 %
Nitrogen	8·2 ,,
Potash	1·3 ,,
Phosphorus pentoxide...	3·8 ,,

Fish manure or *fish guano.*—The bodies of fish are highly nitrogenous and their bones in particular contain large quantities of phosphates. They therefore form a valuable manure and are often used whenever, through an unusual glut in the market, the price falls sufficiently. Then, too, the refuse of fish—their heads, bones, and other offal—is now manufactured into manure, especially in Norway. In America the refuse from the manufacture of Menhaden oil is an important manure. The flesh of whales is also used as manure. In general the most objectionable ingredient in fish guano is the oil, which prevents or hinders the fermentation and decay of the manure by repelling water. The following table shows the average amounts of fertilising material in various kinds of fish manure:—

	Norwegian fish guano.	Raw fish refuse.	Cod guano.	American dried fish.
Water	8·0 %	50·0 %	6·2 %	12·8 %
Nitrogen	9·0 ,,	3·0 ,,	9·0 ,,	7·3 ,,
Calcium phosphate ...	22·0 ,,	3·8 ,,	26·0 ,,	18·2 ,,
Oil		up to 15·0 ,,		

Sea-weed, which is plentiful on some coasts, forms a cheap and valuable manure. It has one great advantage—its rapidity of decomposition, which causes it to be a quick-acting manure. Its composition may be gathered from the following analyses:—

	I.	II.	III.	IV.
Water	80·44	77·94	77·0	81·5 %
Organic matter ...	9·25	18·12	20·0	—
Ash	10·31	3·94	3·0	—
Nitrogen	0·45	0·3	0·38	0·73
Potash	1·95	0·65	0·30	1·50
Phosphorus pentoxide ...	0·47	0·10	0·15	0·18

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* Bulletin 15, U.S. Dept. of Agriculture, 1893.

I. Mixed weed from the Orkney Islands (Anderson).
II. Rock weed, American (Storer).
III. Various varieties of Fucus (Marchand).
IV. Mixed weed (American).

From the above analyses it will be seen that sea-weed is comparable as a manure with farm-yard manure, being, however, slightly deficient in phosphates. It has the advantage over farm-yard manure of being more easily fermented and quite free from the seeds of weeds, which are often abundant in the latter product.

An account of sea-weed as a manure, giving analyses of many specimens of different varieties and the relative values of it and other manures, by Hendrick, appeared in the Transactions of the Highland and Agricultural Society of Scotland, Vol. X. (1898).

The following is a brief summary of the analyses:—

	Black wrack.		Drift weed.	Dulse.
Collected at	Helensburgh.	Stonehaven.	Turnberry.	Oban.
Water	70·78 %	74·99 %	79·00 %	78·20 %
Organic matter ...	23·08 ,,	19·15 ,,	14·49 ,,	17·23 ,,
Ash	6·14 ,,	5·86 ,,	6·51 ,,	4·57 ,,
Phosphorus pentoxide	0·09 ,,	0·09 ,,	0·18 ,,	0·07 ,,
Potash	1·38 ,,	0·85 ,,	1·69 ,,	1·67 ,,
Nitrogen	0·76 ,,	0·51 ,,	0·62 ,,	0·74 ,,

In the field experiments it was found that sea-weed gave with potatoes quite as good results as an equal weight of farm-yard manure and that the application of superphosphate further increased the crop, confirming the statement just made that sea-weed is an excellent organic general manure, though deficient in phosphates.

Dried blood from slaughter-houses is occasionally used as a manure. Sometimes the blood is simply evaporated at a steam heat, in which case the residue can easily be ground to powder. Sometimes the clot only of blood is employed, the clot being produced either by simple separation by a filter or settling, or by the addition of acid or iron salts to the blood.

The following table will show the fertilising value of various commercial forms:—

	Sheep's blood.	Clot of ox blood.	Dried blood.
Water	87·4 %	30·56 %	12·50 %
Organic matter	11·4 ,,	51·43 ,,	87·5 ,,
Ash	1·2 ,,	18·01	
Nitrogen	1·5 ,,	5·9 ,,	10·52 ,,
Phosphorus pentoxide	0·03 ,,	1·0 ,,	1·91 ,,

Blood easily decomposes in the soil, and its nitrogen and phosphoric acid soon become available to the plant. It gives excellent results with wheat.

Bones are an important manure and are used in many forms. They form the hard framework of the body of an animal and are largely composed of mineral matter—mainly phosphate of lime. In addition there are, in fresh or "green" bones, about 30 % of organic matter, containing, perhaps, 3 to 4 % nitrogen, and a certain amount of fat. This last ingredient is objectionable, since it hinders the decomposition of the organic matter after the bones are applied to the soil, partly mechanically and partly, perhaps, by forming a lime soap which gives an impervious crust to each fragment. Moreover, it renders the grinding or disintegration of the material more difficult. For this reason, and also in order to extract gelatine from the bones, they are often submitted to the action of steam under pressure; they are thus robbed of a large portion of their fat and some of their nitrogenous matter, and are rendered much more friable and more susceptible to processes of putrefaction and decay.

Bones when applied to the soil in large fragments only slowly become assimilable, remaining almost unchanged in some cases, especially on clay soils, for years. They are therefore always now reduced to small fragments before being applied, being graded according to their degree of fineness, as "half-inch bones," "crushed bones," "bone dust," "bone meal," and "bone flour." Sometimes bones are treated with acid, when the calcium phosphate dissolves, and the organic matter, from which glue is made, is left behind. From the acid solution, by the action of lime, the calcium phosphate can be precipitated and the dried product is sometimes sold as "precipitated bone flour."

Large quantities of bones are obtained from towns and they are now imported from America and Africa. They are slow in action and their effect upon a soil often extends over several years. In order to render their action more rapid they are often converted into superphosphate or "dissolved bones," which will be described hereafter.

Bone ash is imported from South America; it of course is a purely mineral manure, the organic matter having been removed. Occasionally bones are fermented by moistening them with urine and leaving them exposed to the air.

The following analyses will show the composition of various commercial products from bones:—

	Raw bones.	Fermented Bones.	Steamed bone meal: average.	Bone ash.
Water	11·06	12·02	7·00	6·70
Organic matter ...	30·48	28·71	20·00	—
Calcium phosphate	50·69	49·28	64·00	73·52
Calcium carbonates and undetermined	5·02	8·92	7·30	10·09
Alkali salts	2·25		0·70	
Sand	0·50	1·07	2·00	9·69
	100·00	100·00	100·00	100·00
Nitrogen ...	3·61	3·47	2·5	—

Another product from bones is "*bone black*," used in decolourising liquids, *e.g.*, sugar syrup; this consists of about 10% finely divided carbon, mingled with the mineral constituents of bone, often containing 75—80% calcium phosphate. It is made by heating bones in closed retorts, and after it is so clogged with colouring substances as to be useless for decolourising purposes it is used under the name of "spent char" as a manure, especially as it then contains a small quantity of nitrogen.

Meat meal or meat guano.—This is the dried refuse, with bones, from the manufacture of "extract of meat," &c., reduced to fine powder. A similar product is obtained by drying the offal from slaughter-houses, &c., also, in Germany particularly, by drying the carcasses of horses or cattle that have died from disease. Usually the fat and gelatine are first removed by steaming. Various other bye-products, *e.g.*, the refuse from the manufacture of "oleomargarine," from the manufacture of tallow, &c., &c., are also used for the same purpose. These products are usually fairly free from grease and contain their fertilising materials in a readily fermentable form. The following table gives their average content of valuable ingredients :—

	Meat meal.	German flesh meal.	Oleomargarine refuse.	American tankage from tallow refuse.
Water	10·0%	28·0%	8·5%	10·0%
Nitrogen ...	7·0%	9·7%	12·1%	6·7%
Calcium phosphate	27·0%	13·7%	1·9%	2·6%

Woollen waste, shoddy manure.—After wool has been spun into yarn, woven into a fabric, and worn, the rags are torn to pieces by appropriate machinery and the wool fibre again converted into cloth. This process may go on several times, until finally the fibres, known as "shoddy," become so short that they will no longer hold together. They then constitute "shoddy waste," or shoddy manure, and are useful as a source of nitrogen.

Such manure is variable in composition, according to the treatment which the wool has undergone and the amount of oily substances (used in the cloth manufacture) left in it. The following analyses have been published :—

	I.	II.	III.	IV.
Water ...	7·9%	15·8%	19·9%	—
Nitrogen ...	7·0%	6·5%	6 to 8%	17·0%
Potash ...	0·3%	1·2%		
Phosphorus pentoxide	0·4%	0·35%	Ash = 16·7%	

I. English commercial "ground wool."
II. American wool waste.
III. Shoddy manure of high quality.
IV. Average of pure wool.

Substances of similar composition, sometimes used as nitrogenous manures, are hair from tanneries and horn chips.

Hair contains about 10 to 14% nitrogen, horn shavings about the same.

An American product—horn and hoof waste—contains on the average—

Water	10·17 %
Nitrogen	13·25 %
Phosphorus pentoxide ...	1·83 %

Wool, hair, and horn suffer decomposition in the soil only very slowly; consequently they are not quick in their action, but afford a slow supply of nitrogen for a long period, in some cases for five or six years. They are used in the preparation of certain "mixed manures," and especially in the cultivation of hops. Feathers, which resemble hair in composition, are also used as manure in Ireland.

Soot.—The soot collected from the imperfect combustion of coal contains a portion of the nitrogen of the coal in the form of ammonium salts and as organic nitrogenous compounds of an amine character. Its usefulness as a manure depends upon the nitrogen which it contains; this varies from very little up to 3 or 4 %; on an average perhaps 1·8 or 2 % will be present. Soot is useful as an insecticide.

Oil-cakes.—These, the residue of husks, &c., left after the oil is expressed from certain seeds, are often highly nitrogenous and generally contain considerable quantities of phosphates and potash, indeed, of all forms of plant food. Usually they are used as food for animals; but in some cases, owing to the presence in the seed of poisonous or unpalatable substances, they are only fit for manurial purposes.

Rape, mustard, cotton, and castor cakes are the principal ones used for manure, and of these cotton cake but rarely. The percentages of the important constituents in such cakes are given in the following table:—

	Indian rape cake.	Cotton-seed meal: undecorticated.	Castor cake.
Water	12·0	—	9·5
Nitrogen	5·5	4·3	5·5
Potash	—	1·5	1·1
Phosphorus pentoxide ...	—	3·1	1·7
Oil	10·3	5·0	4·0

These substances decompose slowly in the soil, so that they are not quick-acting manures. They give better results as a rule on clay soils than on light sandy ones.

When the oil has been extracted by solvents the cake is of greater value as a manure, since not only is it richer in the proportion of valuable ingredients, but the absence of oily matter permits of more ready access of water and thus favours oxidation.

CHAPTER VII.

Manures.—*Continued.*

In the previous chapter the chief organic manures have been described; it remains to consider the other substances, generally of mineral or artificial origin, which are employed as fertilisers. They may be conveniently divided into four groups:—

I. Nitrogenous manures.
II. Phosphatic manures.
III. Potash manures.
IV. Miscellaneous.

Many of the organic manures already described contain variable quantities of all the chief manurial substances, but those about to be dealt with are, as a rule, intended to supply only one important item of plant food. Their employment gives the farmer, therefore, the power of applying exactly what he thinks may be necessary, without the introduction of other plant food with which his land may already be abundantly provided. Their general introduction into farming practice has thus rendered easy a far more scientific treatment of the soil than was possible with complex manures only.

I. NITROGENOUS MANURES.—These include the two important substances sodium nitrate and ammonium sulphate, also the less abundant and more expensive potassium nitrate.

Sodium Nitrate, "Chili Saltpetre," occurs in the enormous nitrate deposits of Peru, Chili, and Bolivia. It is found in rainless districts and comparatively near the surface, covering a huge desert devoid of both animal and vegetable life. The raw product, known as *caliche*, is found beneath a covering consisting of two layers, the upper one of sand and gypsum and the lower of baked clay and gravel; beneath the *caliche* is a soft earth known as *cova*. The thickness of the *caliche* varies from a few inches to 12 feet. It is extracted by boring through the upper layers and introducing a charge of gunpowder, which, when fired, exposes a considerable quantity of the material. It is then broken up by means of picks and carried to the refinery.[*] There it is purified by crystallization. This is done by dissolving in water by the aid of heat, allowing the solution to settle, and then running it into tanks, where, on cooling, crystals of sodium nitrate are deposited. The mother liquid is then run off the crystalline mass and treated with sodium sulphite and sodium bisulphite (made on the spot) in large wooden tanks lined with pitch. A precipitation of iodine then takes place by the decomposition of the sodium iodate always present in the *caliche*. The reaction is—

$$2NaIO_3+3Na_2SO_3+2NaHSO_3=5Na_2SO_4+I_2+H_2O.$$

The iodine is then purified by sublimation and forms an important source of profit.

The crystals of nitrate are slightly rinsed with water to wash out the mother liquor adhering to them and are then dried in the sun. The average composition of the product as it leaves the works is said to be—

Sodium nitrate	96·75 %
Water	2·10 %
Sodium chloride	0·75 %
Sulphates	0·30 %
Insoluble matter	0·10 %

The proportion of iodine obtained is about 50 grammes per 100 kilogrammes of crude nitrate[†].

The composition of the *caliche* varies greatly, and as a rule the larger the proportion of sodium nitrate present the less iodine does it contain. It is usual to mix the various qualities so that the mixture becomes fairly constant in composition—

Earth, stones, &c.	50 %
Sodium nitrate	35 %
Magnesium, calcium, and sodium chlorides ...	10 %
Water, sulphates, and other salts	5 %

Associated with the nitrate in the *caliche* a large number of different salts have been detected, including sulphates, nitrates, chlorides, iodates, and borates of calcium, magnesium, and sodium. There are also traces of chromium, existing probably as calcium chromate.*

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[*] See article by Aikman in "Blackwood's Magazine," March, 1892, and Report on the Nitrate Trade of Chili, Jour. Soc. Chem. Ind. 1890, 664.

[†] *v.* Report on the Nitrate Trade of Chili by Consul-General Walker, 1890.

Pure sodium nitrate is a white crystalline salt containing no water of crystallization, but generally holding a small quantity of hygroscopic moisture. Indeed, in moist air it is deliquescent. In addition to its use as a manure it finds application in the arts as a source of nitric acid and in the manufacture of gunpowder and of potassium nitrate.

The product supplied for agricultural purposes is supposed to contain 95% or over of real sodium nitrate and thus to yield more than 15·6% of nitrogen. Being extremely soluble and diffusible it is at once available to plants and should only be applied when the crop is sufficiently grown to be capable of assimilating it; otherwise, since it is not retained by any constituent of the soil, considerable loss in the drainage may occur.

In 1897† Sjollema found that in many cases in Holland and Belgium, rye was damaged by the application of "nitrate of soda." On investigation he found that the injury was due to the presence, in the nitrate, of perchlorates. In a number of samples examined he found from 0·14 to 6·79% of perchloric acid (ClO_4). By direct experiment he showed that potassium and sodium perchlorates retard germination and cause the leaves of plants to which they are applied to become yellow.

Other investigations have confirmed these results; *e.g.*, Zaharia as a result of an examination of 206 samples of Chili saltpetre at Halle found one sample containing between 5 and 6%, one 3 to 4%, three 2 to 3%, eleven 1·5 to 2%, thirty-nine 1·0 to 1·5%, while the remaining 151 contained less than 1% of perchlorate‡.

Maercker§ in 107 samples of Chili saltpetre found—

	Nitrogen.	Sodium nitrate.	Sodium perchlorate.
Maximum ...	15·6%	94·7%	5·64%
Minimum ...	13·8%	83·8%	0·27%
Mean ...	15·1%	91·6%	0·94%

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* Buchanan, Jour. Soc. Chem. Ind. 1893, 128.

† Annales Agronomiques 1897, 328; Jour. Chem. Soc. 1897, abst. ii., 585.

‡ Bied. Centr. 1899, 511; Jour. Chem. Soc. 1899, 799.

§ Jahresbericht über Agricultur-Chemie 1899, 105.

and Crispo[*] gives the following analyses of specimens of Chili saltpetre from the same cargoes as those which had been observed to have a harmful effect upon plants :—

	I.	II.	III.	IV.
Nitrogen ...	15·44	15·70	15·40	15·40
Water	1·97	1·69	3·05	3·32
Sodium nitrite ...	0·00054	0·00054	0·00054	0·00054
Sodium chloride ...	0·15	0·17	1·55	1·09
Magnesia ...	0·089	0·077	0·217	0·25
Sodium iodate ...	0·004	0·015	0·040	0·033
Sodium perchlorate	1·04	0·97	0·93	0·90

That sodium perchlorate has an injurious effect on most plants appears certain, but the quantity which is permissible in sodium nitrate is a matter on which much diversity of opinion appears to exist.

Zaharia (just quoted) found that solutions containing less than 0·1 % of perchlorate had little or no effect upon the germination of beet, rye, and wheat, though oats were affected. The seedlings, however, were injured by even much weaker solutions, oats being most affected, then rye, wheat, and lastly barley; a 0·001 % solution had no effect on barley and wheat, but injured oats. He found that the application of nitrate containing 1 % perchlorate decreased the production of grain and straw about 4 %, while nitrate containing 2 % lessened the grain by 25 % and affected the straw to an even greater extent.

De Caluwe[†] found that sodium perchlorate was more poisonous than the potassium salt, rye and maize being the most susceptible crops. The application of 150 grammes of sodium nitrate to the square metre gave a crop of 6·7 kilogrammes with pure nitrate, but when the nitrate contained 2·67 % of sodium perchlorate the yield was only 3·35 kilogrammes, while nitrate containing 4 to 5 % of the perchlorate proved fatal in all cases.

Sodium nitrate is the most important artificial source of nitrogen and has taken the place, to a great extent, of guano; as the supplies of the latter substance have now been almost exhausted, it naturally occurs to one that a similar fate may soon befall the supplies of nitrate. Various estimates of the total available nitrate in the deposits of Chili, Peru, and Bolivia have been made, ranging from 63,000.000 to 178,000,000 English tons. In 1895 the total export from Chili reached 1,220,000 tons, while the following table gives the world's consumption for the past years:—

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[*] Annales Agronomiques 1898, 92.

[†] Bull. Assoc. Belge des Chim. 12, 363; Jour. Soc. Chem. Ind. 1899, 1141.

	1896.	1897.	1898.	1899.
Europe (continent)...	805,000	867,500	900,000	1,017,000
United Kingdom ...	105,000	108,000	132,000	123,000
United States ...	105,000	110,000	142,000	160,000
Other countries ...	8,000	14,500	12,000	30,000
Total ...	1,023,000	1,100,000	1,186,000	1,330,000

The average prices at Liverpool have been—

£7 15s. 5d. per ton in 1897.
£7 11s. 3d. ,, 1898.
£7 19s. 7d. ,, 1899.*

Ammonium Sulphate.—When organic nitrogenous bodies are submitted to destructive distillation, *i.e.*, heated strongly without access of air, the nitrogen which they contain is to a great extent expelled as ammonia, which is carried away in the vapours and gases simultaneously produced. The most important operation of this kind is the distillation of coal, and it is mainly from this source that the supplies of ammonium compounds are obtained. Ordinary coal contains a little over 1 % of nitrogen, and when burnt in the usual way this nitrogen escapes into the air, mainly in the free state. When coal is distilled, however, a portion of the nitrogen is liberated as ammonia and is found in the so-called "ammoniacal liquor" which results from the cooling of the vapours evolved during the distillation. Coal is distilled for the production of coal-gas for illuminating purposes and also, in a somewhat different manner, for the manufacture of the special coke used in iron smelting. Gas works and coke ovens thus provide a large share of the "ammoniacal liquor" which forms the raw material for the manufacture of ammonium salts. A similar operation is the distillation of the bituminous shales used in the Scotch paraffin industry, while the production of pig iron is sometimes effected by the use of coal instead of coke, and in this case arrangements are sometimes made by which the ammonia and tarry products which are evolved during the first stages of the heating of the coal may be collected. Another source of ammonia is the liquid condensed from the "producer gas" and "water gas" formed when a current of air or steam is forced over red-hot coal.

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* Jour. Soc. Chem. Ind. 1900, 88.

The product obtained in any of these processes is a complex mixture consisting of an aqueous solution of ammonium sulphide, carbonate, thiosulphate, thiocyanate, and chloride.

The composition of gas liquor may be gathered from the following analyses of products obtained from the Leeds gas works, I. in 1883* and II. in January, 1901† :—

	I.	II.	
Total ammonia ...	20·45	19·45	grammes per litre
Total sulphur ...	3·92	4·22	,, ,,
Ammonium sulphide ...	3·03	3·72	,, ,,
,, carbonate ...	39·16	33·97	,, ,,
,, chloride ...	14·23	12·61	,, ,,
,, thiocyanate	1·80	0·93	,, ,,
,, sulphate ...	0·19	0·63	,, ,,
,, thiosulphate	2·80	3·84	,, ,,
,, ferrocyanide	0·41	trace	,, ,,

Organic bases and other substances are also present, but were not estimated.

In order to prepare a marketable commodity from this liquid it is heated and lime is added. The ammonia volatilises partly as carbonate and sulphide, partly as free ammonia, and is received in sulphuric acid, whereby sulphate of ammonia is formed, and carbon dioxide, sulphuretted hydrogen, and other gases are evolved; these are led away and suitably disposed of. The liquid is then evaporated in leaden pans until it crystallizes. Formerly the ammoniacal liquor was sometimes directly neutralised with sulphuric acid and the solution evaporated. In this case the resulting sulphate was impure and contained the highly objectionable thiocyanate, NH_4CNS, which is very injurious to vegetable life. Its detection in a specimen of sulphate is easy, its presence being at once indicated by the production of a blood-red colouration when the solution is mixed with a little ferric chloride solution. In the modern product this impurity is rarely present. Another possible impurity of importance is arsenic, which may be present in the sulphuric acid; it, too, is objectionable, being highly poisonous both to animals and plants.

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* S. Dyson, J.S.C.I. 1883, 229; J.C.S. 1884, abst. 928.

† A. W. Cooke, J.S.C.I. 1901. This sample represented the yield of three works, a total of about 6000 tons of liquor. For an account of the composition of gas liquor obtained at various stages of the distillation, &c., v. L. T. Wright, Journal of Gas Lighting 48, 280; or abstract in Jour. Soc. Chem. Ind. 1886, 655.

The sulphuric acid used in the manufacture of sulphate of ammonia ought to be either the arsenic-free acid specially prepared for the purpose from brimstone, or pyrites acid which has been freed from arsenic. Certain forms of Spanish pyrites give acid containing as much as 1% or even 2% of arsenious oxide and have just recently been brought into prominence from the numerous cases of arsenic poisoning by beer, the arsenic being traced to the sulphuric acid used in the preparation of the glucose added to the wort in the brewing. Arsenic, if present in large quantities, usually imparts a yellow colour (due to As_2S_3 [?]) to the ammonium sulphate.

Theoretically, coal containing 1·3% of nitrogen ought to yield about 149lb. of sulphate of ammonia per ton; but in practice the coal used in gas works and for coke-making only gives about 20lb. of sulphate per ton of coal, owing to a large portion of the nitrogen being retained in the coke, some being evolved as free nitrogen and some as pyridine, pyrrol, and other nitrogenous tarry products.

In the manufacture of producer and water gas, especially by some of the most recent methods (*e.g.*, by the "Mond" process), where the temperature is kept low, the yield of sulphate may amount to three or four times that just given.

The magnitude of the ammonium sulphate manufacture may be judged from the following table, which gives the production in the United Kingdom during the years 1896, 1897, 1898, and 1899:—

	1896. Tons.	1897. Tons.	1898. Tons.	1899. Tons.
From gas works ...	127,498	132,724	129,590	133,000
,, iron works ...	16,511	17,779	17,935	18,700
,, shale works ...	37,822	37,153	37,264	37,300
,, "producer," coke, and carbonising works	9,078	10,624	11,568	13,000
Total	190,909	198,280	196,357	202,000[*]

Of the 202,000 tons produced in 1899, 140,370 tons were exported. In 1900 the total production was estimated at 213,000 tons, in 1901 at 220,000 tons.

The average price of sulphate of ammonia during 1899 is given as £11 5s. 9¾d. per ton, as against £9 9s. 7½d. in 1898 and £7 18s. 4¾d. in 1897.[†] Its present price (March, 1902) is about £11 11s. 0d.

Numerous experiments on the relative advantages of nitrate of soda and sulphate of ammonia as sources of nitrogen have been made. The general results may be summarised thus:—

1. Nitrate of soda is quicker in its action, being already capable of yielding its nitrogen to the crop. Sulphate of ammonia must first undergo nitrification in the soil before it can be utilised to any extent by the plant. For this process to occur it is necessary that some basic material (generally calcium carbonate) be present in order to (1) combine with the sulphuric acid of the sulphate (the calcium sulphate formed is carried off in the drainage water) and (2) to assist in nitrification by forming calcium nitrate. For these reasons sulphate of ammonia can only successfully be applied to soil containing a sufficiency of calcium carbonate, and its repeated application entails a considerable loss of lime (equal to 100 of calcium carbonate for every 132 of sulphate of ammonia applied, or if the lime required for nitrification be included, twice this amount) in the drainage water—

$$(NH_4)_2SO_4 + CaCO_3 = CaSO_4 + (NH_4)_2CO_3 \text{ and}$$
$$(NH_4)_2CO_3 + 4O_2 + CaCO_3 = Ca(NO_3)_2 + 2CO_2 + 4H_2O.$$

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[*] For later statistics see J.S.C.I. 1902, 146.

[†] Jour. Soc. Chem. Ind. 1900, 87.

Soils deficient in lime compounds can be more suitably manured with nitrate of soda.

2. Nitrate of soda is easily washed out of the soil by rain and in wet seasons a considerable amount of it is lost. It should only be applied when the plant can assimilate it. Sulphate of ammonia, though equally soluble in water, is not washed out by rain to any appreciable extent, but is held by the humus and perhaps by the hydrated silicates and the ferric hydroxide until nitrification occurs. Sulphate of ammonia is therefore preferable in wet seasons and gives the best results when applied at the time of sowing, or even before. Nitrification can only take place in the presence of sufficient, and is favoured by increased, moisture, short of complete saturation, so that in dry seasons sulphate of ammonia is not so suitable as nitrate of soda.
3. On soils very rich in calcium carbonate, ammonium sulphate, if used as top-dressing, may suffer decomposition, with loss by volatilisation of ammonium carbonate, especially in dry weather. This loss can be prevented by ploughing or harrowing the sulphate into the soil immediately after its application.
4. Both nitrate of soda and sulphate of ammonia will only yield the best results when the soil is abundantly supplied with the necessary mineral constituents of plant food.
5. Nitrate of soda, not being absorbed by any of the constituents of the soil, penetrates into the subsoil and thus favours the production of deep roots, which gives the plant a better chance of finding mineral food and of withstanding drought.
6. Nitrate of soda is best applied in several small dressings, while sulphate of ammonia may generally be applied in one. The usual quantities are from 1 to 1½cwt. of the former and 100 to 150℔. of the latter per acre, but with certain crops, *e.g.*, mangolds and potatoes, larger quantities may be used.

Potassium Nitrate.—This substance, though doubly valuable as a fertiliser, inasmuch as it supplies both potassium and nitrogen in a directly available form, is too expensive to be used as a manure except under special circumstances. Like sodium nitrate, it occurs as a deposit in rainless districts in the tropics, especially in India. It was also made by the so-called "Nitre plantations" in France and other countries. These consisted of heaps of earth, old mortar, road scrapings rich in calcium carbonate, &c., mixed with decomposing animal matter, protected from the rain by a shed and placed on an impervious floor. The heap was watered periodically with urine, liquid manure, or other liquid rich in animal nitrogenous matter. Nitrification under these favourable conditions took place rapidly and the liquid draining away contained large quantities of nitrates of potassium and calcium. At long intervals the heap was lixiviated with water and the solution mixed with wood ashes or potassium carbonate, when calcium carbonate was precipitated and removed and potassium nitrate was extracted from the solution by evaporation and crystallization—

$$K_2CO_3 + Ca(NO_3)_2 = CaCO_3 + 2KNO_3.$$

It is probable that the saltpetre of India owes its origin to a similar action of nitrification, the potash coming from the minerals in the soil.

Potassium nitrate is now made in large quantities from sodium nitrate and potassium chloride, which when mixed in solution and evaporated yield, first sodium chloride crystals, and then, on cooling, potassium nitrate.

The properties of saltpetre are well known and need not be described here.

II. PHOSPHATIC MANURES.—Several of the manures already described are mainly valued for the phosphates they contain; this is the case with the non-nitrogenous guanos, steamed and burnt bones, &c. There are other sources of phosphoric acid of greater importance, which must now be described. Before mentioning the manures themselves, it may be advisable to briefly describe the various forms in which phosphoric acid occurs in fertilisers. These are—

(1) As tricalcium phosphate, $Ca_3(PO_4)_2$.
(2) ,, dicalcium phosphate, $Ca_2H_2(PO_4)_2$ or $CaHPO_4$.
(3) ,, monocalcium hydrogen phosphate, $CaH_4(PO_4)_2$.
(4) ,, free phosphoric acid, H_3PO_4.
(5) ,, ferric or aluminium phosphate, $FePO_4$ or $AlPO_4$.
(6) ,, tetracalcium phosphate, $Ca_4P_2O_9$.

Tricalcium Phosphate is a white, almost insoluble substance which dissolves easily in acids. It is the form in which phosphoric acid occurs in bones, in most mineral phosphates, and to a large extent in guano. The solubility of the salt in water free from carbon dioxide and air is, according to Pollacci,* 0·0098 gramme per litre at 12·5°, or, if the phosphate be dried at 25° instead of moist, 0·0181 gramme; if the water be saturated with carbon dioxide it dissolves 0·1605 at 10·5°. The solubility and particularly the rate of solution depend greatly upon the physical condition of the phosphate, being favoured by fineness of subdivision, porosity, and an amorphous state.

The most important mineral phosphate is *apatite*, which has a composition corresponding to the formula $3Ca_3P_2O_8.CaCl_2$, or $3Ca_3P_2O_8.CaF_2$, the varieties being sometimes distinguished by the names—chlor-apatite and fluo-apatite; this substance occurs as hexagonal crystals, often of a green or yellow colour. Many of the mineral phosphates consist of what is practically amorphous apatite.

Dicalcium Phosphate, $CaHPO_4$, when prepared by precipitation, is a white solid containing 2 molecules of water. It is only slightly soluble in water, but its solubility is greatly increased by the presence of many neutral salts, *e g.*, ammonium citrate. It probably is more readily dissolved by the acid juices of plants' roots than is tricalcium phosphate. By long boiling with water it is said to yield a mixture of tricalcium and monocalcium phosphates.

$$4CaHPO_4 = Ca_3P_2O_8 + CaH_4P_2O_8.$$

Monocalcium Phosphate, $CaH_4P_2O_8.H_2O$, can be obtained in thin rhombic plates. It is best prepared by dissolving dicalcium phosphate in phosphoric acid and washing the crystals obtained with alcohol and ether.* It is not hygroscopic if free from excess of phosphoric acid. When treated with a small quantity of water a portion of the salt is decomposed, with the formation of dicalcium phosphate as a precipitate and free phosphoric acid; but with larger quantities of water or in the presence of free phosphoric acid this does not occur.

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* Jour. Chem. Soc. 1897, abst. ii. 260.

Free Phosphoric Acid, H_3PO_4, is a thick, semi-solid mass, of sp. gr. 1·88, formed by decomposing, say, calcium phosphate with sulphuric acid—

$$Ca_3P_2O_8+3H_2SO_4=3CaSO_4+2H_3PO_4.$$

It is soluble to practically any extent in water.

Ferric Phosphate, $FePO_4$, and **Aluminium Phosphate** are practically insoluble in water and, unlike tricalcium phosphate and most other phosphates, are not dissolved to any appreciable extent by weak vegetable acids, *e.g.*, acetic acid. Consequently they are not easily available to plants and possess little value as manurial ingredients.

Tetracalcium Phosphate, $Ca_4P_2O_9$, is found in the slag produced in the dephosphorisation of cast-iron by the Basic Bessemer or Basic Siemens process. It is practically insoluble in water, but dissolves in many saline solutions. It is therefore available as a plant food.

The chief varieties of phosphatic manures yet to be described are—

Coprolites.
Phosphorites, of which there are many varieties.
Redonda phosphate.
Mineral superphosphates.
Bone superphosphate.
Basic slag.

Coprolites are concretionary nodules found in the chalk or other deposits in the South of England and in France; they are believed to be the fossilised excrements or intestinal deposits of extinct animals which fed upon fish.

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* Stocklasa, Jour Chem. Soc. 1890, abst. 695.

They were formerly of great importance and are still largely used. Their composition varies considerably, the chief constituents being—

Calcium phosphate ...	50 to 65%
Calcium carbonate ...	20 to 25%
Silica, &c.	10 to 20%

They are sometimes used raw in a finely divided state, but generally converted into "superphosphate."

Of mineral phosphates or **phosphorites** there are many varieties, the most important being Norwegian, Canadian, Sombrero, Belgian, Carolina, Florida, and Somme. These are only occasionally employed in the raw state, but are mainly used in the preparation of "mineral superphosphates." They all consist essentially of more or less impure apatite, some containing calcium chloride, others calcium fluoride, and some both compounds. In the process of manufacture of superphosphate the first variety is much preferred, for reasons which will be mentioned shortly.

Another factor of importance in gauging the value of a mineral phosphate is the proportion of iron and aluminium which it contains.

The extent and growth of the phosphate mining industry may be seen from the following table, giving the total production in tons of raw phosphates in 1880 and 1890*:—

	1880.	1890.
England (coprolites)...	30,000	20,000
France	125,000	370,000
Belgium	15,000	200,000
Germany	25,000	30,000
Norway	5,000	10,000
Canada	7,500	26,000
South Carolina ...	187,000	537,000
Florida	—	40,000
Spain	40,000	—
West Indies ...	35,000	50,000
Other sources ...	30,000	20,000
Total	500,000	1,303,000

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* Bulletin No. 15, United States Dept. of Agriculture, 1893.

Since 1890 the increase has been maintained, as is seen by the following return of the production in the United States alone*:—

	1895.	1896.	1897.	1898.	1899.
Tons...	1,098,668	862,671	1,014,322	1,231,758	1,710,000

Large quantities now come from Algeria, the output in 1898 being over 223,000 tons.†

The following table gives the average composition of a number of mineral phosphates :—

	Tricalcium phosphate.	Calcium fluoride.
Coprolites	50—60 %	
Belgian phosphate ...	33 %	
Florida, pebbles	60—65 %	
South Carolina	58 %	1—2 %
Lalm or Nassau (Germany)	30—75 %	
Canadian	80—95 %	

Redonda Phosphate (Leeward Islands) consists largely of aluminium phosphate and is therefore, in its raw state, not of much value. Lalm phosphate also contains a considerable quantity of ferric oxide and alumina, which lowers its value.

Mineral Superphosphates.—It is for the manufacture of these substances that the mineral phosphates are chiefly used, for in their raw state the latter are too insoluble to be of much value as fertilisers. In an extremely fine state of division, however, they become more available and are sometimes used.

Superphosphate is made by treating the mineral with sulphuric acid, when a replacement of phosphoric acid by sulphuric acid takes place, calcium sulphate and free phosphoric acid being formed—

$$Ca_3P_2O_8 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4.$$

The sulphuric acid also acts upon calcium carbonate, calcium chloride or fluoride, and oxides of iron and aluminium, if these be present, evolving carbon dioxide, hydrochloric or hydrofluoric acid—

$$CaCO_3 + H_2SO_4 = CaSO_4 + H_2O + CO_2$$
$$CaCl_2 + H_2SO_4 = CaSO_4 + 2HCl$$

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[*] Jour. Soc. Chem. Ind. 1899, 190, and 1900, 86.

[†] J.S.C.I. 1899, 315.

$$\begin{aligned} CaF_2+H_2SO_4 &= CaSO_4+2HF \\ Al_2O_3+3H_2SO_4 &= Al_2(SO_4)_3+3H_2O \\ Fe_2O_3+3H_2SO_4 &= Fe_2(SO_4)_3+3H_2O. \end{aligned}$$

These various reactions consume a portion of the sulphuric acid and, in many cases, are produced before the action upon the calcium phosphate begins.

In general the amount of sulphuric acid used is only sufficient to liberate phosphoric acid from a portion of the calcium phosphate, and a subsequent interaction then occurs between the phosphoric acid so liberated and the unchanged tricalcium phosphate—

$$Ca_3P_2O_8+4H_3PO_4=3CaH_4P_2O_8$$

—thus producing monocalcium tetrahydrogen phosphate.

Superphosphates thus consist essentially of a mixture of

Calcium sulphate, $CaSO_4.2H_2O$,
Calcium tetrahydrogen phosphate, $CaH_4P_2O_8$,
and generally Tricalcium phosphate, $Ca_3P_2O_8$.

In many samples, aluminium sulphate and ferrous or ferric sulphate are also present in small proportions.

The important constituent is, of course, the monocalcium phosphate, $CaH_4P_2O_8$, which is soluble in water, the tricalcium phosphate being of much less value. On keeping, many superphosphates show a reduction in the amount of phosphate soluble in water, and an increase in the insoluble phosphoric acid. This may be caused in two ways—

(a) By the interaction of the monocalcium phosphate and the tricalcium phosphate leading to the formation of dicalcium phosphate*—

$$CaH_4P_2O_8+Ca_3P_2O_8=4CaHPO_4$$
$$(\text{or } 2Ca_2H_2P_2O_8).$$

(b) By the formation of ferric and aluminium phosphate by the action of the monocalcium phosphate upon the iron and aluminium sulphates—

$$Al_2(SO_4)_3+CaH_4P_2O_8=2AlPO_4+CaSO_4+2H_2SO_4$$
$$Fe_2(SO_4)_3+CaH_4P_2O_8=2FePO_4+CaSO_4+2H_2SO_4.$$

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* This substance is present even in fresh superphosphate, so that "reverted" phosphate is to some extent a misleading name, inasmuch as some of the substance so-called has never been present in a soluble form. The amount of phosphates of this character is determined by taking advantage of their solubility in ammonium citrate (*v.* Chap. VIII.); the name "citrate-soluble" phosphorus pentoxide would therefore be preferable to the names already mentioned.

The free sulphuric acid thus formed would be used in acting upon some of the unchanged $Ca_3P_2O_8$ as before.

In either case a quantity of phosphoric acid formerly in the soluble condition as $CaH_4P_2O_8$ would pass into an insoluble form. Such phosphoric acid and phosphates are often spoken of as "retrograde," "reduced," or "reverted" phosphate. They generally possess a higher manurial value than tricalcium phosphate.

In the process of manufacturing superphosphate the ground phosphate is mixed with the suitable quantity of sulphuric acid (chamber acid of sp. gr. 1·55) in "mixers" made of wood lined with lead, or of iron lined with fire-brick, and provided with stirrers rotated by gearing. The carbon dioxide, hydrofluoric or hydrochloric acid, and steam evolved by the action are led away into a "scrubber" or "condenser," in which the steam condenses and absorbs the acids. The prevention of their escape into the atmosphere is enforced by law. When the lining of the "mixer" is fire-clay (highly silicious) phosphates containing calcium fluoride cause the production of gaseous silicon fluoride—

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF$$
$$SiO_2 + 4HF = SiF_4 + 2H_2O.$$

The silicon fluoride escapes with the other gases and on contact with the condensed steam produces a gelatinous precipitate of silica and a solution of hydrofluosilicic acid, H_2SiF_6—

$$3SiF_4 + 4H_2O = SiO_4H_4 + 2H_2SiF_6.$$

The presence of fluorine in phosphates is thus attended with the production of the very corrosive hydrofluoric acid, the consequent wear and corrosion of the fire-clay lining, and the accumulation of the very bulky, gelatinous silicic acid in the condenser, tending to choke it. The bye-product, hydrofluosilicic acid, possesses antiseptic properties and can be used as a preservative of farm-yard manure. When the admixture of the acid and phosphate is complete, the contents of the "mixer" are transferred to pits or "dens" made of brick-work or masonry. The mixture at this stage is usually semi-fluid and runs easily. In the "dens" the union of the calcium sulphate with water takes place, resulting in the formation of crystals of the same composition as the mineral gypsum, $CaSO_4.2H_2O$. This causes the product to "set" or "dry," and after this it is ground in suitable mills and screened and is ready for the market.

"Double superphosphate" is sometimes made by preparing phosphoric acid by the action of excess of acid upon one portion of the phosphate, removing the greater part of the calcium sulphate, and adding the phosphoric acid to another portion of the original phosphate, thus converting the tricalcium into monocalcium phosphate—

$$Ca_3P_2O_8 + 4H_8PO_4 = 3CaH_4P_2O_8.$$

Such a product is very concentrated and may contain as much as 40% of phosphoric acid, nearly all in the soluble form.

Manures similar to superphosphate are made by the action of sulphuric acid upon bone-ash, bones, or guano. These resemble mineral superphosphates so far as the state of existence of their phosphoric acid is concerned, but may, of course, contain nitrogenous constituents.

The following table gives the amount of the most important fertilising ingredients in various forms of manures of this class, expressed in the usual conventional way:—

	Mineral superphosphate. %	Dissolved bones. %	Dissolved Peruvian guano. %	Dissolved bone-ash. %
Monocalcium phosphate...	15—20	9—15	9—13	20—29
=tricalcium phosphate rendered soluble ...	24—32	14—24	14—20	31—45
Insoluble phosphates ...	1—4	16—21	5—12	1—6
Calcium sulphate ($+2H_2O$)	52—54	28—33	16—30	46—51
Alkaline salts	2—2·5	2·5—3·5	6—10	1—2·5
Ammonia	—	2—3·5	7—10	0—0·2

A word of explanation as to the commercial methods of expressing analytical results may be here given. It is the custom to indicate by, say, "24 per cent. soluble phosphates" that 24 is the amount of tricalcium phosphate which contains the same quantity of phosphoric acid as is present in the soluble (monocalcium) phosphates contained in 100 parts of manure.

$$\begin{array}{lccc} \text{Since} & Ca_3P_2O_8 & \text{corresponds to} & CaH_4P_2O_8 \\ & \underbrace{120+62+128} & ,, & \underbrace{40+4+62+128} \\ & 310 & ,, & 234 \end{array}$$

the amount of real calcium tetrahydrogen phosphate corresponding to "24% soluble" would be $24\times\frac{234}{310}=18{\cdot}1$; but even this is not what is meant, for by "monocalcium phosphate" in the trade the substance CaP_2O_6 (really calcium meta-phosphate, which is not present in manures) is understood; so that as this contains the same amount of P_2O_5 as $Ca_3P_2O_8$ the connection becomes—

$$\begin{array}{ccc} CaP_2O_6 & \text{corresponds to} & Ca_3P_2O_8 \\ \underbrace{40+62+96} & ,, & \underbrace{120+62+128} \\ 198 & ,, & 310 \end{array}$$

Consequently, in the trade, the quantity of monocalcium phosphate equivalent to "24% soluble phosphates" or to "24% bone phosphate rendered soluble," as it is sometimes more explicitly described, is given by—

$$24\times\frac{198}{310}=15{\cdot}4\%.$$

By the term "insoluble phosphates" in the above analyses is meant the amount of tricalcium phosphate present as such, together with that equivalent to the dicalcium phosphate or "reverted" phosphate. The latter is much more valuable than the former and in recent analyses the quantities of each present are given (see Chapter VIII.).

Reference may here be made to a recently patented manure to which the contradictory name of *basic superphosphate* has been given. This is a product obtained by adding 15 parts of slaked lime to 85 parts of good superphosphate, thoroughly mixing the two, and allowing them to stand at least 24 hours. A dry, bulky powder is thus produced, which, it is claimed, has many advantages over basic slag.* Some of the analyses advanced in support of the claim were, in the present writer's opinion, far from conclusive. To quote one as an example: A comparison was made between the new manure and basic slag as to their solubility: the following numbers were given:—

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* Hughes, Jour. Soc. Chem. Ind. 1901, 325.

	Relative solubility in cold water after 48 hours.	
	"Basic super."	Basic slag.
Portion soluble	66·80	6·60
Portion insoluble (after burning)	33·20	93·40
Soluble lime	22·28	4·70

No phosphate soluble in water.

In the first place, since phosphoric acid is the valued ingredient in both manures and in neither case was any dissolved in water, the comparison as a criterion of their manurial value is useless. Next, the "basic super." is highly hydrated, while the basic slag is practically anhydrous, and the "portion soluble" in the table evidently includes the water present (for it is the difference between 100 and the "portion insoluble, after burning"). Moreover, of the "portion soluble" a large proportion consists of the comparatively worthless calcium sulphate, in which state also much of the "soluble lime" exists.

The new manure may probably produce a better effect than superphosphate upon soils deficient in calcium carbonate or other basic material, but it would certainly seem preferable either to use basic slag on such soils, or to apply the lime and superphosphate separately and thus secure the advantage of their more uniform distribution in the soil, which their solubility in water (while separate) ensures.

Basic Slag, or **Thomas Phosphate,** is now one of the cheapest and best sources of phosphoric acid. It results as a bye-product in the manufacture of steel from pig-iron rich in phosphorus. In order that the student may clearly understand its origin, it will perhaps be advisable to briefly review the chemistry of the processes used in the production of steel.

Until 1856 steel was made by the laborious and expensive process of first obtaining *pig-iron* or *cast-iron*, in which are numerous impurities (as is seen from the subjoined analysis), removing these impurities, including almost the whole of the carbon, by *refining* and *puddling*, and so obtaining *wrought-iron*, which is almost pure iron, and lastly causing this, after it had been rolled out into thin bars, to combine with the requisite quantity of carbon by the process known as *cementation,* in which the bars of wrought-iron are heated in a closed iron case with powdered charcoal for several days. The iron under this treatment was converted into steel. The process was so costly and tedious that steel commanded a very high price and was only used for special purposes.

Analyses of pig-iron, wrought-iron, and steel—

	Pig-iron (good quality).	Wrought-iron (Low Moor).	Steel (Bessemer rails).
Graphite	3·180	—	—
Combined carbon ...	0·750	0·016	0·352
Silicon	1·960	0·122	0·053
Phosphorus ...	0·040	0·106	0·061
Sulphur	0·018	0·104	0·055
Manganese ...	3·460	0·280	0·384
Copper	0·080	—	trace
Iron	90·501	99·372	99·095
	99·989	100·000	100·000

In 1856 Bessemer introduced his process for making steel directly from pig-iron. This consists in running the molten pig-iron into an egg-shaped vessel mounted on trunnions and constructed of boiler plates lined with a particularly infusible fire-clay known as *ganister* and consisting of almost pure silica. At the bottom of this vessel, known as a *converter,* are holes through which air can be blown by means of a pipe passing through one of the trunnions. The blast of air passing through the molten iron oxidises the carbon, silicon, sulphur, and part of the iron, producing thereby a higher temperature, so that although pure iron has a much higher melting point than cast-iron, the contents of the converter do not solidify. The carbon by its oxidation produces carbon monoxide, which burns at the mouth of the converter, and the end of the operation can be detected by the sudden dying down of this flame ; the contents of the converter then consist of practically molten wrought-iron. It is converted into steel by the addition of a suitable quantity of a particular variety of cast-iron known as "*spiegeleisen,*" which contains a high percentage of carbon. The metal is then poured out of the converter.

This process quite revolutionised the iron industry, and steel became so cheap that it almost replaced iron. The Bessemer process, however, could only be applied to pig-iron fairly free from phosphorus, for the process does not remove any phosphorus, and if steel contains much of this element its properties are so altered that it becomes valueless.

The following table shows the change in the composition of the metal in the "Bessemer converter" (acid lining):—

	Original pig-iron.	After 9 minutes.	Before addition of spiegeleisen.	Finished steel.
Carbon ...	3·270 %	1·550 %	0·097 %	0·566 %
Silicon ...	1·052	0·635	0·020	0·030
Sulphur ...	0·014	trace	trace	trace
Phosphorus ...	0·048	0 064	0·067	0·055
Manganese ...	0·086	trace	trace	0·309

It will be noticed that there is no reduction in the amount of phosphorus, but rather an increase, while the sulphur, carbon, and silicon are almost entirely removed.

About 1878-79 a modification in the method of working the Bessemer process was introduced by Thomas and Gilchrist, by which pig-iron containing high percentages of phosphorus could be successfully converted into steel of good quality. Their improvement consisted in lining the converter with lime or a mixture of lime and magnesia and the introduction of freshly burnt lime into the converter. They found that under these circumstances the phosphorus in the pig-iron (existing in combination with iron as phosphide) was oxidised by the air after the carbon had been completely removed, and the phosphoric acid so formed united with the lime and magnesia of the basic lining to form a slag which floated on the molten iron. The rest of the process is conducted as in the original Bessemer or "acid" process. This improvement was of great importance, especially to iron masters in districts where the iron ore contained large quantities of phosphates.

The following table gives the data in the case of the Thomas-Gilchrist or Basic-Bessemer process, the pig-iron used being so rich in phosphorus as to be quite unfit for use by the ordinary Bessemer-process:—

	Original pig-iron.	After 12min.	After 14min. End of ordinary blow.	After 16½min. End of after blow.	Steel.
Carbon ...	3·57 %	0·88 %	0·07 %	trace	0·124 %
Silicon ...	1·70	0·01	trace	nil	0·030
Phosphorus ...	1·57	1·42	1·22	0·08 %	0·220
Manganese ...	0·71	0·27	0·12	trace	0·270
Sulphur ...	0·06	0·05	0·05	0·05	0·040

It will be seen from the above table that the silicon is first oxidised and removed, then the carbon, and not until practically all the carbon is removed does the removal of the phosphorus begin.

The slag obtained by the basic process therefore receives its phosphate in the last few minutes of the process. This is seen from the following figures :—

	Time from commencement of the blow.				Slag at the end of the process.
	6min.	12min.	14½min.	16½min.	
Silica ...	42·60 %	35·60 %	33·00 %	16·60 %	18·60 %
Phosphorus pentoxide ...	0·15	2·61	5·66	16·03	13·87
Iron ...	2·00	4·80	6·15	11·35	7·10

The process resulted in a still further cheapening of steel. For some years the slag produced, though it was known to contain a considerable quantity of phosphoric acid, was regarded as simply a waste product of no use. It was thought that the oxide of iron present in the slag would prevent the phosphoric acid from being available to plants. Its use as a manure for soils poor in lime was suggested about 1882,* as it was found that a considerable proportion of the phosphoric acid in the slag was in such a state of combination as allowed of its easy solubility in ammonium citrate solution. This led to numerous trials of the slag, and many of these proving highly satisfactory its use rapidly extended and has now assumed gigantic proportions.

The composition of the slag necessarily varies somewhat, but its main constituents are represented in the following analysis of a specimen†:—

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* Maercker, Bied. Centr. 1882, 490; Jour. Chem. Soc. 1882, abst. 1229.
† Stead and Ridsdale, Jour. Chem. Soc. 1887, Trans. 601.

	%
Lime	45·04
Magnesia	6·42
Alumina	1·50
Ferrous oxide	2·10
Ferric oxide	15·42
Manganous oxide	3·50
Vanadious oxide	1·35
Silica	5·80
Sulphur	0·32
Calcium	0·40
Phosphorus pentoxide ...	18·10
	99·95

The sulphur present seems to exist as a sulphide, probably of calcium. The phosphoric acid is present as tetracalcium phosphate, $Ca_4P_2O_9$, a substance which sometimes occurs nearly pure as crystals imbedded in the slag.

According to Hoyermann and Wagner* the citrate-solubility of the phosphoric acid in basic slag is greatly increased if the slag be fused with sand. Wagner states that the citrate-solubility (by which he judges of the availability) of the basic slag of commerce varies from 100 to 40 %, and that a high solubility depends upon the presence of at least a certain percentage of silica. Ridsdale† denies this and states that the only function of the silica is the neutralising of a certain proportion of the free lime of the slag and thus preventing the action of this upon the citrate solution employed.

Many attempts to improve basic slag as a manure have been made, some directed to the removal of the iron, others the sulphur, while others have attempted to render the phosphoric acid more soluble, by treatment with sulphuric acid. Practically all these attempts have been abandoned, and the only process through which the slag is passed is that of grinding. This must be thoroughly done, for it is found that the availability of the phosphoric acid depends very largely upon the fineness of subdivision. A sample should contain at least 80 or 90 % of powder which passes through a sieve of 100 meshes

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[*] Chem. Zeitung 1895, 1511.

[†] Jour. Soc. Chem. Ind. 1895, 170.

to the linear inch, *i.e.*, 10,000 to the square inch. Thomas phosphate has given excellent results, especially in soils somewhat deficient in lime and rich in organic matter.

The magnitude of the trade in basic slag may be gathered from the accompanying table giving the quantity sold as a fertiliser in Europe during 1899.*

	Sold. Tons.	Used in the country. Tons.	Exported. Tons.
Germany ...	786,000	730,000	56,000
Great Britain ...	256,000	110,000	146,000
France ...	198,000	198,000	—
Belgium ...	112,000	80,000	32,000
Austria Hungary	64,000	90,000	—†
Total ...	1,416,000	1,208,000	234,000

So successful has Thomas phosphate proved as a manure that lately a product known as "artificial Thomas phosphate meal" has been made in Germany by a method devised by Wolters. Raw mineral phosphates are fused with silicious materials, *e.g.*, sand or glass, and chalk or limestone, and a product resembling basic slag is thus obtained. In another preparation potash is introduced. According to analyses of the two products by Maercker‡ they contain—

	I.	II.
Total phosphorus pentoxide ...	15·50 %	16·89 %
Phosphorus pentoxide soluble in citrate solution	14·52 %	15·38 %
Lime	41·80 %	—
Silica	26·83 %	—
Potash	—	13·10 %

Another product of somewhat similar character as to citrate-solubility of its phosphates is the so-called Wiborgh phosphate, another German product. It is prepared by heating the crude phosphate (mainly apatite), containing some felspar, with soda-ash, to about 1000° C.

The reactions are said to be—

$$3(Ca_3P_2O_8).CaF_2 + 3Na_2CO_3$$
$$= 2Na_2O.10CaO.3P_2O_5 + 2NaF + 3CO_2$$
$$K_2O.Al_2O_3.6SiO_2 + 2Na_2CO_3 = K_2O.2Na_2O.Al_2O_3.6SiO_2 + 2CO_2$$

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* Engineering and Mining Journal, 69, 648. Jour. Soc. Chem. Ind. 1900, 574.

† 26,000 tons were imported, chiefly from Germany.

‡ Jahresbericht Agricultur-Chemie 1899, 129.

The double sodium-calcium phosphate has a constitution similar to tetracalcium phosphate, and like that substance is soluble in ammonium citrate solution (up to 95 % of the total phosphoric acid). The triple silicate of sodium, potassium, and aluminium contains its potash in a more readily available form than the original felspar. The composition of the residue, which is easily powdered, is*—

	%
Phosphorus pentoxide ...	27·01
Silica	9·99
Sulphur trioxide	0·27
Potash	1·54
Soda	14·69
Lime	38·12
Magnesia	2·88
Iron oxide and alumina ...	4·50
Fluorine and loss	1·00
	100·00

It is probable that a recently devised, continuous process of dephosphorising pig-iron (Talbot's patent) may lead to an increased production of basic slag.

III. POTASH MANURES.—Potash is much more widely distributed and less frequently deficient in soils than are nitrogen and phosphoric acid. Potash manures, therefore, are less often used than those already described; although certain crops, *e.g.*, potatoes, are greatly helped by their application. Formerly the chief source of potash, both for manurial and other purposes, was the ash left when twigs, leaves, &c., of plants are burnt. Potash occurs in such material as carbonate, and plant ashes are still used to some extent as a manure. They contain the other mineral ingredients, phosphates, lime, &c., but they are especially rich in potash. The chief source of potash is now the immense saline deposits at Stassfurt, and other deposits of a similar kind have been discovered in Thuringia, Brunswick, and Mecklenburg.

These deposits, in some cases hundreds of feet in thickness, rest upon beds of rock-salt, and it was in boring for the rock-salt that they were discovered about 1857. At first they were regarded as useless, as is indicated by the name "Abraumsalzen" (rubbish salts), by which they are still sometimes known. About five or six years later they were worked as a source of potash compounds, and now enormous quantities are annually raised and furnish almost all the potash required in the arts as well as in agriculture.

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* Nilson, Jahresbericht Agric.-Chem. 1899, 127.

The chief compounds are classed under the following mineralogical names:—

Sylvine, KCl.
Sylvinite, a mixture of sylvine, rock-salt, and kainite.
Carnallite, $MgCl_2KCl.6H_2O$.
Schœnite (Picromerite), $MgSO_4.K_2SO_4.6H_2O$.
Kieserite, $MgSO_4.H_2O$ (mixed with carnallite).
Kainite, $MgSO_4.KCl.3H_2O$, or $MgSO_4.K_2SO_4MgCl_2.6H_2O$.
Polyhalite, $K_2SO_4.2CaSO_4.MgSO_4.H_2O$.

The substances do not occur in the pure form indicated by these formulæ, but are more or less mixed with each other and especially with rock-salt. Carnallite is, by far, the most abundant.

The output of Stassfurt salts is now regulated by a syndicate, who limit the production and fix the prices of the various salts.

In 1898 the quantities in tons produced and sent out to the various countries were as follows:—

	Potassium chloride, 80 %	Potassium sulphate, 90 %	Calcined potassium and mag. sulphate.	Kainite and sylvinite.	Carnallite and kieserite.
Germany	70,877	679	136	722,115	60,793
Austria & Switzerland	3,844	20	—	17,302	—
Great Britain ...	13,481	1,818	352	26,311	229
France	14,870	1,957	108	12,241	141
Belgium and Holland	8,723	1,089	967	37,118	6,798
Italy	3,924	337	—	149	—
Sweden and Denmark	4,048	1	—	51,364	1
Russia	2,379	577	—	8,004	30
North America ...	54,272	9,308	8,945	176,065	—
Spain and Portugal ...	1,119	521	—	2,364	—
Other countries ...	446	1,474	27	3,193	—
Total ...	177,983	17,781	10,533	1,056,226	67,982

Of the 70,877 tons of chloride used in Germany only about 1528 tons were employed in agriculture, the rest being used as the raw material for the production of other potash salts. Of the 107,107 tons exported, however, about 64,000 tons were employed for agricultural purposes, the extra cost of this material over the raw products, kainite, &c., being compensated by the greater cheapness of its transport, owing to its high potassium content. The same is true of potassium sulphate, which in Germany is chiefly used in the preparation of alum, not more than a third of the quantity given in the table being used as a fertiliser, while of that exported more than seven-eighths of the total is employed in agriculture.*

In this country the products employed are mainly kainite, the calcined double sulphate of potash and magnesia, and the "muriate of potash." For special horticultural purposes pure sulphate of potash and nitrate of potash are also employed.

The important potash manures contain their potassium either as chloride or sulphate. The chloride has the advantage in being more diffusible in the soil; but in most other respects the sulphate is preferable. As in the case of other soluble manures, interaction between the potassium salt and the calcium and other compounds in the soil begins immediately, resulting in the formation of calcium chloride or sulphate. The former has an injurious action upon plants, while the latter is harmless or probably beneficial. Moreover, when potassium chloride is applied in large quantities, the salt as a whole seems to be absorbed by some plants, and in the case of tobacco, for example, the ash left when the dried plant is burnt contains the easily fusible potassium chloride. This acts as a fire-proofing material to some extent and prevents the proper burning of the tobacco; potassium sulphate yields a crop containg no such fusible ash constituent. In the case of clover, corn, and grass, however, potassium chloride appears to have little or no harmful effect.

Potash manures are most needed on light sandy or calcareous soils and are seldom required on clay land. Potatoes, grass land, and leguminous crops are particularly benefited by potash manures. They are best applied in the autumn or winter so as to be well diffused through the soil before the plant requires them. Little loss through drainage need be feared.

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* Sammel-Austellung der Deutschen Chemischen Industrie, Paris Exhibition, 1900.

Muriate of potash is usually sold as guaranteed to contain 80% KCl (equivalent to about 51% K_2O).

The double sulphate of magnesium and potassium actually occurs crystallised with six molecules of water—as Schönit—$MgSO_4.K_2SO_4.6H_2O$, and then contains theoretically about 44% of K_2SO_4: practically, 42% is about the average. The commercial product is calcined, whereby a portion of the water is expelled, and the residue then contains on the average 48% K_2SO_4 (equivalent to 26% K_2O). It usually contains about 2% lime and 2½% Cl.

Sylvinite contains varying quantities of common salt, water, &c., and is not often used as a manure in England, though it is imported into America. Its average content of potassium is said to correspond to 16 or 17% K_2O.

Sulphate of potash is usually of from 90 to 95% purity (49 to 51% K_2O), and is too high priced to be often employed in agriculture.

Kainite is the most widely used potash manure. This substance, the exact constitution of which has not yet been determined, is the mineral itself, crushed or ground. Its composition varies, doubtless owing to its admixture with other minerals, especially carnallite and rock-salt, occurring in association with it.

The proportion of potash varies from 12 to 20%, being usually near the lower figure. The sodium chloride varies from 25 to 45%. It also contains lime, magnesia, and sulphates. The presence of much magnesium chloride is objectionable, since this compound is deliquescent.

The following table gives the average composition of the various commercial preparations[*] :—

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[*] **Lierke, Agricultural Chemist to the Verkaufs-Syndicat der Kaliwerke, Leopoldshall-Stassfurt.**

AVERAGE PERCENTAGE COMPOSITION OF THE PRINCIPAL STASSFURT POTASH SALTS.

Name of product.	Potassium sulphate.	Potassium chloride.	Magnesium sulphate.	Magnesium chloride.	Sodium chloride.	Calcium sulphate.	Insoluble matter.	Water.	Total potash K_2O.
A. Crude Salts (Minerals)									
1. Kainite	21·3	2·0	14·5	12·4	34·6	1·7	0·8	12·7	12·8
2. Carnallite	—	15·5	12·1	21·5	22·4	1·9	0·5	26·1	9·8
3. Rock Kieserite	—	11·8	21·5	17·2	26·7	0·8	1·3	20·7	7·5
4. Sylvinite	1·5	26·3	2·4	2·6	56·7	2·8	3·2	4·5	17·4
B. Concentrated Salts. *(Manufactured products)*									
1. Sulphate of Potash 96 % ...	97·2	0·3	0·7	0·4	0·2	0·3	0·2	0·7	52·7
1. Sulphate of Potash 90 % ...	90·6	1·6	2·7	1·0	1·2	0·4	0·3	2·2	49·9
2. Sulphate of Potash and Magnesia...	50·4	—	34·0	—	2·5	0·9	0·6	11·6	27·2
3. Muriate of Potash 90—95 % ...	—	91·7	0·2	0·2	7·1	—	0·2	0·6	57·9
3. Muriate of Potash 80—85 % ...	—	83·5	0·4	0·3	14·5	—	0·2	1·1	52·7
3. Muriate of Potash 70—75 % ...	1·7	72·5	0·8	0·6	21·2	0·2	0·5	2·5	46·7
4. Potash Manure Salts .. ... Minimum 20 % K_2O.	2·0	31·6	10·6	5·3	40·2	2·1	4·0	4·2	21·0
5. Potash Manure Salts ... ... Minimum 30 % K_2O.	1·2	47·6	9·4	4·8	26·2	2·2	3·5	5·1	30·6

IV. MISCELLANEOUS MANURES.—Under this heading may be classed substances which contain none of the three chief manurial ingredients, potash, phosphoric acid, and nitrogen, but convey to the soil some other constituent of plant food, or effect by their action upon the soil the liberation of some necessary plant food from the insoluble and unavailable condition. Among the most important are the following:—

Common salt.
Gypsum.
Lime and chalk.
Ferrous sulphate.
Gas lime.

Common Salt is usually regarded as possessing no real manurial value, but as owing what merit it possesses to its action in promoting the decomposition of the potash, lime, and magnesia compounds already present in the soil. It has an undoubtedly good effect on certain crops, particularly mangolds and cabbages. It probably also has an effect, in common with all soluble salts, upon the physical properties of the soil and upon its power of retaining water. Waste salt from fish-curing, bacon-curing, &c., has a value because of the nitrogen and potash which it contains, these substances being derived partly from the organic matter and partly from the saltpetre which is also used in "curing." Salt is sometimes used in mixed manures; solutions of common salt undoubtedly have a greater solvent action than water upon phosphates and silicates.

Gypsum, or **Land Plaster** (American), $CaSO_4.2H_2O$, has been found to give good results when applied to fields of clover or turnips. It may act as a source of sulphur, but in all probability its action is indirect, and its good effects are due to the liberation of potash from the double silicates in the soil. Its action in promoting nitrification has already been mentioned.* Where superphosphates (of which calcium sulphate is a large constituent) are employed, its application is not required.

Lime, Chalk, Marl, or **Limestone.**—These substances—

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* *v.* p. 69.

consisting mainly of oxide, hydrate, or carbonate of lime, but always containing small and varying quantities of magnesia, phosphoric acid, and iron oxide—are employed as manures. The important function performed by calcium carbonate in the process of nitrification has already been discussed.*

The chief effect of the application of lime or its carbonate to a soil is to accelerate nitrification and thus to enable the crop to draw upon the nitrogenous stores already present in the soil. Another action of value is its neutralising effect upon the organic acids in peaty soils, the presence of which is unfavourable to any but coarse, undesirable plants. It also acts by replacing the potash in the silicates. Although caustic lime (*i.e.*, CaO or CaH_2O_2) speedily becomes converted into the carbonate when applied to the soil, it always has a more energetic action than chalk or limestone. This is due to its solubility producing a more uniform distribution throughout the soil before precipitation as calcium carbonate occurs than it is possible to obtain by the mere mechanical admixture of the soil with even finely powdered chalk or limestone.

Lime made from magnesian limestone and therefore containing magnesia is not so suitable for agricultural purposes as a purer product. This is usually stated to be due to the fact that so long as the bases are in the caustic state, *i.e.*, as hydroxide, they have an injurious effect upon vegetation, and magnesia is said to combine with carbon dioxide much less readily than lime does. Consequently a lime containing much magnesia may retain its caustic condition (because of the MgH_2O_2) in the soil for a much longer time than a pure lime would under the same conditions.

Too heavy or too frequent dressings with lime produce harm by exhausting the stores of nitrogenous matters contained in the humus of the soil.

The very valuable flocculating effects of lime upon clay have been already discussed.†

Ferrous Sulphate, $FeSO_4.7H_2O$, known commercially as "copperas" and "green vitriol," is not often used as a manure. Iron is usually sufficiently abundant in a soil. Griffiths‡ greatly extols the application of small quantities (up to ½cwt. per acre) of ferrous sulphate as a top-dressing for meadows, and also for beans, cabbages, potatoes, mangolds, and cereals. He found that the iron sulphate increased the amount of chlorophyll in the green portions of the plant, that the crops were larger, richer in solid matter, albuminoids, and phosphates, and that the growth of mosses, &c., was hindered or prevented. He also claims that the iron, to a certain extent, performs the functions of potash in the plant, and that in many cases ferrous sulphate may advantageously be substituted for kainite or other potash manures. Continental experimenters have confirmed in many instances the claims of ferrous sulphate as a manure. In addition to its specific action, it, like other sulphates, probably supplies sulphur.

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* *v.* p. 67. † *v.* p. 51 ‡ Jour. Chem. Soc. 1885, Trans. 54; 1886, Trans. 121.

Gas Lime.—In the preparation of coal-gas various sulphur compounds are expelled by distillation from the coal, and though a considerable proportion of these are collected in the ammonia-liquor and tar, some find their way into the gas, and inasmuch as they are highly objectionable there, purification has to be resorted to. One of the common methods of removing sulphuretted hydrogen and carbon disulphide from the coal gas is to pass it into chambers containing layers of slaked lime, when the following reactions occur:—

$$CaH_2O_2 + H_2S = CaS + 2H_2O$$

$$CaS + CS_2 = CaCS_3.$$

Simultaneously, the carbon dioxide is also removed—

$$CaH_2O_2 + CO_2 = CaCO_3 + H_2O.$$

Small quantities of cyanogen are also absorbed.

The spent lime is a complex mixture—calcium sulphide, sulpho-carbonate, sulphite, carbonate, thiocyanate, and hydrate being the chief ingredients, with varying small quantities of ammonia, cyanides, ferrocyanides, &c. Many of these compounds are powerful plant poisons and *fresh* gas lime is extremely destructive to all plant life. On exposure to air and rain, especially if mixed with soil, absorption of oxygen takes place, and the sulphides, sulphites, &c., are oxidised first into thiosulphate and finally into sulphate—

$$CO_2 + 2CaS + 3O = \underset{\text{Calcium thiosulphate.}}{CaS_2O_3} + CaCO_3.$$

$$CaSO_3 + O = CaSO_4.$$

$$CaS_2O_3 + 2O_2 + CaH_2O_2 = 2CaSO_4 + H_2O.$$

The composition of fresh gas lime (from London gas works) is, according to Guyard*—

	%
Calcium hydrate	15·10
,, carbonate	24·20
,, thiosulphate	11·80
,, sulphide	6·90
,, oxysulphide	3·20
,, sulphate	0·25
,, sulphite	1·50
,, cyanide	0·25
Iron sulphide	0·55
Sulphur	4·30
Silica	1·80
Alumina	0·70
Magnesia	trace
Tar	0·25
Water	29·20
	100·00

If the unoxidised sulphur compounds remain in gas lime until its application to the land, great harm and sometimes total destruction of vegetation may ensue. In view, then, of the uncertainty of its action its general use cannot be recommended.

Copper Sulphate.—Though this substance cannot act as a direct plant food and has seldom (or perhaps never) been used as a manure, some results obtained when spraying crops for disease or for the purpose of destroying charlock, &c., seem to indicate that it acts as a powerful stimulus to the growth of certain plants, for in many cases distinctly beneficial effects have been observed from its use in the case of grain crops and potatoes, where no charlock or disease was present.

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* Bull. Soc. Chim. xxv. 103; Jour. Chem. Soc. 1876, ii. 123.

CHAPTER VIII.

THE ANALYSIS OF MANURES.

IN this chapter, before discussing very briefly some of the methods used for the determination of the valuable constituents of manures, a short account of the usual methods of expressing the results of a chemical analysis of manures will be given. Some of these methods are purely conventional and involve the use of certain terms which are no longer used in the same sense in modern scientific nomenclature. Take, for example, a superphosphate; the usual old-fashioned method of expressing its composition is as follows:—

ANALYSIS OF A SUPERPHOSPHATE.

	%
Soluble phosphates	
(equal to bone phosphate rendered soluble) ...	
Insoluble phosphate	
Hydrated sulphate of lime	
Organic matter and water	
Alkaline salts	
Silica	

The explanation of some of these terms has already been given (*v.* p. 156), but may perhaps with advantage be repeated here.

By "soluble phosphates" in the above analysis is meant all the phosphates soluble in water, expressed as mono-calcium phosphate (not, as would be correct, as $CaH_4P_2O_8$, but totally falsely as CaP_2O_6, which is the formula for calcium metaphosphate). Consequently the percentage amount of "soluble phosphates," in order to give the equivalent amount of "bone-phosphate," *i.e.*, $Ca_3P_2O_8$, must be multiplied by $120+62+128=310$, and divided by $40+62+96=198$.

By "insoluble phosphate" in the analysis is meant the total of tricalcium (and trimagnesium) phosphate, $Ca_3P_2O_8$ (insoluble in solution of ammonium citrate), and dicalcium phosphate, $Ca_2H_2P_2O_8$ ($=CaHPO_4$), together with the phosphoric acid in combination with iron and aluminium (soluble in solution of ammonium citrate), all expressed in terms of tricalcium phosphate. The phosphoric acid soluble in ammonium citrate solution is known as "reverted," "retrograde," or "reduced."

The "hydrated sulphate of lime" obviously refers to the compound analogous to gypsum, $CaSO.2H_2O$.

"Organic matter and water" requires no explanation; it is loss on ignition after deducting the water contained in the "hydrated sulphate of lime," which would also be expelled; why this allowance is made for mere water of crystallization in the case of calcium sulphate and no allowance for the necessary water of constitution of the mono-calcium tetrahydrogen phosphate, $CaH_4P_2O_8$, it is difficult to understand.

"Alkaline salts" is another unsatisfactory item; it is hard to say exactly what it means.

"Silica" usually represents the matter insoluble in acids and often consists mainly of real silica, SiO_2, though it may contain other mineral fragments.

A much more scientific and in every way more satisfactory way of reporting such an analysis, adopted in more recent work, is as follows:—

		%
Total phosphorus pentoxide		
of which is	Soluble	
	"Reverted," "reduced," "retrograde," or, better, "citrate soluble" ...	
	Insoluble	
Sulphur trioxide		
Loss on ignition		
Potash (if any)		

In the case of nitrogenous manures it is often the practice to give the nitrogen as equal to —% of ammonia; if the percentage of nitrogen is given as well, this plan is perhaps permissible, but it would be much more intelligible to give the latter than the former. The percentage of ammonia equivalent to the nitrogen present should therefore not be given alone, especially in analyses of organic manures or those containing nitrates. If the nitrogen content be stated, no error as to its state of existence can be conveyed, and its equivalent in ammonia or nitrogen pentoxide is easily calculated, since $N = NH_3 = \frac{N_2O_5}{2}$ or 14 of nitrogen correspond to 17 of ammonia or 54 of nitrogen pentoxide.

The most complete way would be as follows :—

		%
Total nitrogen	... ...	
of which is	Ammoniacal nitrogen	
	Organic nitrogen	
	Nitric nitrogen	

The analysis of a manure is usually directed to the determination of the amounts of one or more of the three substances nitrogen, phosphorus pentoxide, or potash present, and to the detection of the presence, and if necessary the determination of the amount, of any possibly harmful or objectionable ingredients.

The following table gives a list of most of the commercial manures, with their valuable and objectionable ingredients :—

I. NITROGENOUS MANURES.

Name.	Constituents of value.	Harmful constituents.
Dried flesh	Organic nitrogen.	Oily matters.
,, blood ...		
Shoddy and woollen waste		
Hair, horn, and leather waste		
Rape and other oil-seed cakes ...	Organic nitrogen (phosphoric acid).	Oil.
Sulphate of ammonia	Ammoniacal nitrogen.	Thiocyanates, arsenic.
Nitrate of soda ...	Nitric nitrogen.	Perchlorates, chlorides.
Nitrate of potash ...	,, ,, and potash.	
Soot	Ammoniacal and organic nitrogen.	

II. PHOSPHATIC MANURES.

Name.	Constituents of value.	Harmful constituents.
Basic slag	Citrate-soluble phosphorus pentoxide (lime), also degree of fineness of division.	
Phosphorite and coprolites	Insoluble phosphorus pentoxide.	Iron and alumina; fluorides, if for "super." manufacture.
Precipitated phosphate	Ditto.	
Bone ash, bone black...	Ditto.	
Mineral superphosphate	Soluble, insoluble, and citrate-soluble phosphorus pentoxide.	Iron and alumina, arsenic.

III. NITROGENOUS PHOSPHATIC MANURES.

Bone dust and bones...	Insoluble phosphorus pentoxide and organic nitrogen.	Sand.
Spent animal charcoal		
Fish manure ..		Oil, sand.
Nitrogenous guanos ...	Soluble, citrate-soluble, and insoluble phosphorus pentoxide, organic and ammoniacal nitrogen.	
Dissolved ,, ...		Arsenic, excessive quantity of calcium sulphate.
Ammoniated ,, ...		
Dissolved bones ...		

IV. POTASH MANURES.

Potassium chloride and sulphate	Potash.	Excessive quantities of sodium and magnesium chlorides.
Kainite		
Potashes		
Potassium nitrate ...	Potash, nitric nitrogen.	
Refuse from wool scouring	Potash, organic nitrogen.	

In addition, the general manures, *e.g.*, farm-yard manures, sea-weeds, &c., contain all constituents of plant food, together with large quantities of decaying organic matter and water.

For full descriptions of the methods used in the analysis of manures the reader must refer to some treatise on the subject —only an outline can be given here.

Determination of Nitrogen.—The method to be employed depends upon the possible state of existence of the nitrogen in the manure.

Organic Nitrogen, such as occurs in farm-yard manure, sea-weed, guano, fish meal, bones, rape-seed meal and cake, &c. The most satisfactory method is the Kjeldahl process, which may be performed exactly as described under soil analysis, p. 95. The result gives the amount of nitrogen existing as organic compounds and as ammonia, and in most cases a portion of that existing as nitrates. As in soil analysis, the nitric nitrogen can be wholly included if salicylic acid be added (*v.* p. 96).

Ammoniacal Nitrogen.—This can be estimated by distillation with magnesia, MgO, conveniently in a current of steam, and receiving the evolved ammonia in a measured quantity of decinormal sulphuric acid. Potash or soda would also liberate ammonia from ammonium salts, but they would, in addition, decompose a portion of the organic nitrogenous substances, if such were present.

Nitric Nitrogen.—In manures containing a large proportion of this constituent, *e.g.*, sodium nitrate, the determination can conveniently be made by means of Lunge's nitrometer, an instrument in which the volume of nitric oxide, NO, evolved on shaking up the nitrate with strong sulphuric acid and mercury can be measured. Another satisfactory method of determining nitrate is by Schlösing's method with ferrous chloride and hydrochloric acid. Other methods for the determination of nitric nitrogen are based upon its reduction to ammonia and subsequent distillation with alkali. This reduction may be brought about by treatment in alkaline solution with zinc and iron (Möckern's process), or in presence of sulphuric acid by reduced iron (Ulsch's method), or by treatment with a mixture of sulphuric acid, salicylic acid, and sodium thiosulphate (Forster's method).

In many cases nitrate of soda is valued by "refraction," *i.e.*, by determining the total percentage amount of the impurities present. The substances usually present in Chili saltpetre are—moisture, insoluble matter, chlorine, sulphuric acid, magnesia, and perchlorate. These constituents are determined by the usual processes. A word or two may be said about the determination of the perchlorate, a substance whose presence and importance in nitrate has only recently been realised. Five grammes of the dried sample are heated for a quarter of an hour over a Bunsen lamp with 7 or 8 grammes of pure calcium hydroxide in a covered crucible. The mass is then transferred to a measuring flask, made up to 128 c.c. with water, digested for an hour and filtered (3 c.c. is taken as the volume of the undissolved matter, so that 125 c.c. of solution are really taken). To 100 c.c. of the filtrate (= 4 grammes of the sample) dilute nitric acid is added until exactly neutral and the chloride present is then determined by titration with silver nitrate. After deducting the chlorine present, originally as chloride (determined by direct titration without treatment with lime), the chlorine found is calculated to perchlorate.*

In the case of most manures the determinations of the various constituents are made by the usual quantitative methods, but in some cases shorter and easier, though perhaps less accurate, methods are employed. A few of these rapid methods may be mentioned.

Phosphoric Acid.—In the presence of aluminium, iron, and calcium in ordinary analytical work it is generally considered necessary to first precipitate the phosphoric acid with ammonium molybdate, wash the yellow precipitate until the abovementioned metals are removed, redissolve the precipitate in ammonia and precipitate with magnesia mixture. Instead of this somewhat tedious and costly process, by the addition of citric acid to the original solution, followed by magnesia mixture and ammonia, it is possible to keep the iron, aluminium, and lime in solution and obtain all the phosphoric acid as magnesium ammonium phosphate. The method is only suitable when the quantity of phosphoric acid is fairly large and that of iron and aluminium not considerable.

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* Blattner and Brasseur, Chem. Zeitung 1900, 767.

The phosphoric acid of a manure may be present in three states of combination, as already stated:—

1. Water-soluble phosphates.
2. Citrate-soluble phosphates.
3. Insoluble phosphates.

The methods of determining the first and third require little or no explanation. For the second the residue after washing with water is used. It is extracted with a solution of ammonium citrate of specified strength, for a specified time, and at a specified temperature.

The ammonium citrate solution employed is usually of sp. gr. 1·09 at 20° and contains about 370 grammes of crystallized citric acid, neutralised with ammonia, in two litres of water (American), or 333 grammes citric acid in two litres (Petermann), or about 360 grammes (Halle process).

The temperature and time of digestion recommended by different workers varies—30° or 40° for half an hour (Frankland); 50° for half an hour (Halle station); 35° to 40° for one hour (Norway stations); 65° for half an hour (American official chemists).

In any case the liquid is filtered and washed, and the phosphoric acid in the residue determined as usual.

Thus direct determinations are made of—

(1) Phosphoric acid soluble in water.
(2) Total phosphoric acid.
(3) Phosphoric acid insoluble in ammonium citrate.

The difference between (2) and (3) gives the citrate and water-soluble phosphoric acid, and by subtracting (1) the citrate-soluble or "reverted" phosphoric acid is obtained.

In the case of basic slag the tetracalcium phosphate is soluble in citrate solution, but as there is always more or less free lime present, Wagner recommends that sufficient citric acid be added to neutralise the free lime in 5 grammes of the slag, and then 200 c.c. of acid ammonium citrate (made by dissolving 160 grammes of citric acid in water, adding 27·93 grammes of real NH_3 and diluting to 1 litre). After filtering, the phosphorus pentoxide in solution is estimated by separation with ammonium molybdate solution and precipitation by magnesia mixture as usual.

Potassium in presence of sulphuric acid, iron, lime, and magnesia.—Usually the above bases and the sulphuric acid have first to be removed by means of ammonia, ammonium carbonate or oxalate, and barium chloride, necessitating the subsequent removal of the ammonium compounds and excess of barium. By direct addition of platinum chloride to the hydrochloric acid solution of the original substance, evaporation to dryness, and washing, first with a little platinum chloride solution, then with alcohol, next with a 20% solution of ammonium chloride, to which sufficient solid K_2PtCl_6 has been added to saturate it, and lastly again with alcohol, a pure double chloride of potassium and platinum may be obtained.

THE VALUATION OF MANURES FROM ANALYSIS.—From the percentage amounts of the valuable constituents in a manure and its commercial value per ton, it is easy to calculate the cost of the actual valuable ingredient per ℔., or, as is perhaps more usual in this country, "per *unit*," *i.e.*, the value per ton of each per cent.

For example, take nitrate of soda, containing, say, 15·75% nitrogen, and assume its price per ton to be £8.

Nitrogen in this form costs—

$$\frac{8 \times 20 \times 100}{2240 \times 15{\cdot}75} = {\cdot}457\text{s. per ℔.} = 5{\cdot}484\text{d. per ℔.}$$

or its value "per unit" $= \frac{8 \times 20}{15{\cdot}75} = 10{\cdot}2\text{s.} = 10\text{s. } 2\tfrac{1}{2}\text{d.}$

In sulphate of ammonia, containing, say, 24·5 % of "ammonia," equal to 20·2 % nitrogen, if its price be taken at £12 per ton, nitrogen costs—

$$\frac{12 \times 20 \times 100}{2240 \times 20{\cdot}2} = {\cdot}53\text{s. per lb.} = 6{\cdot}36\text{d. per lb.}$$

or its value "per unit" $= \dfrac{12 \times 20}{20{\cdot}2} = 11{\cdot}83\text{s.} = 11\text{s. }10\text{d.}$

The two methods of expressing values are related to each other in a simple manner. It is evident that the price "per unit," since it refers to the price per ton for each per cent. of the constituent in question, is really the price of $\frac{1}{100}$ of a ton of the actual manurial constituent. In other words it is the price of 22·4lb. Obviously the price per lb. multiplied by 22·4 will give the equivalent price "per unit."

In a similar way the value of phosphorus pentoxide and potassium can be calculated from the market prices of the various phosphatic and potash manures. As in the case of nitrogen, the values obtained vary in the case of different manures.

Tables are sometimes published giving the value of the three principal manurial substances per unit in various commercial manures. The table on the following page, calculated from one given in the Transactions of the Highland and Agricultural Society of Scotland, 1900, may serve as an example.

The figures in brackets after the name of the manure indicate the trade guarantees.

In ordinary tables of this kind the values per unit of "ammonia" and "phosphates" (*i.e.*, $Ca_3P_2O_8$) are usually given, and not those of nitrogen and phosphorus pentoxide, as in the following table. The latter plan certainly appears preferable, except on the ground of custom, since such substances as nitrate of soda or any organic manure contain none of their nitrogen in the form of ammonia; and, similarly, superphosphate and basic slag contain most of their phosphorus pentoxide in forms other than tricalcium phosphate. Perhaps the same argument applies to the other manurial constituent—potassium—(though to a less degree), since in some manures it exists as chloride.

Manure.	Price per ton. £	s.	d.		£	s.	d.	Valuable constituent.	Value per unit. s.	d.	Value per ℔ d.
Sulphate of ammonia (24 % ammonia)					12	0	0	Nitrogen	12	0	6½
Nitrate of soda (19 % ammonia)					8	0	0	,,	10	2	5½
Peruvian guano	5	0	0	to	9	0	0	,,	17	0	10¾
								P_2O_5	3	3	1¾
Bone meal	5	10	0	to	6	0	0	Nitrogen	12	0	6½
								P_2O_5 (insoluble)	2	9	1½
Steamed bone flour	4	15	0	to	5	0	0	Nitrogen	12	0	6½
								P_2O_5 (insoluble)	2	9	1½
Dissolved bones	5	5	0	to	5	10	0	Nitrogen	12	0	6½
								P_2O_5 (soluble)	5	5	3
								P_2O_5 (insoluble)	2	9	1½
Superphosphates	2	5	0	to	3	5	0	P_2O_5 (soluble)	4	1	2¼
Thomas slag					1	15	0	P_2O_5 (insoluble)	2	6	1⅓
Muriate of potash (50 % K_2O)					8	15	0	K_2O	3	6	2
Sulphate of potash (27 % K_2O)					5	0	0	K_2O	3	9	2
Kainite (12 % K_2O)					2	0	0	K_2O	3	4	1¾

It may perhaps be useful to give an example of the application of the table of "unit value" to the calculation of the money value of a manure from its analysis.

Suppose a sample of dissolved bones to yield the following numbers on analysis :—

		%
Total phosphorus pentoxide ...		17·1
Soluble ,, ,,	8·6	
Insoluble ,, ,,	8·5	
Nitrogen		2·5

Its value per ton would be calculated as follows :—

% Value "per unit."		£	s.	d.
8·6 × 5/5.	Value of soluble phosphorus pentoxide =	2	6	7
8·5 × 2/9.	,, insoluble ,, ,, =	1	3	4½
2·5 × 12/-.	,, nitrogen ... ... =	1	10	0
		£4	19	11½

In America the plan of expressing the trade value of manurial ingredients in price per pound is general. The following table (quoted by Wiley from Bulletin 51, 1894, of the Mass. Agric. Exp. Station) gives the estimated trade values :—

	Cents per ℔.	or d.
Nitrogen in ammonium salts	19	9½
,, ,, nitrates	14½	7¼
,, ,, dry and fine fish, meat, blood, &c. ...	18½	9¼
,, ,, fine bone and tankage	16½	8¼
,, ,, cotton-seed meal, castor cake, &c. ...	15	7½
,, ,, medium bone and tankage	12	6
,, ,, coarse bone and tankage	7	3½
,, ,, hair, horn, and coarse fish refuse ...	6	3
Phosphorus pentoxide, soluble in water	6	3
,, ,, ,, ,, ammonium citrate	5½	2¾
,, ,, in fine bone and tankage ...	5½	2¾
,, ,, ,, medium bone and tankage	3	1½
,, ,, ,, coarse bone and tankage	2	1
,, ,, ,, fish, oil-seed cakes, and wood ashes ...	5	2½
,, ,, ,, mixed fertilisers, insoluble in ammonium citrate	2	1

Potash in sulphates and mixtures free from chlorine	5	2½
,, ,, chloride	4½	2¼

—while the manurial constituents of foods are valued as follows:—

Organic nitrogen ...	15 cents or	7½d. per lb.
Phosphorus pentoxide ...	5 ,,	2½d. ,,
Potash	5 ,,	2½d. ,,

It must be clearly understood that the above method of valuing manures is based only upon trade prices and in no way depends upon the results of agricultural experience.

Tables have been constructed giving the relative value of the same manurial constituent when applied to land in various forms as measured by the increase in the crop produced. For example, according to experiments by Wagner in 1886 with wheat, barley, and flax, the effect of the various forms of phosphatic manures upon plants abundantly supplied with potash and nitrogen are represented by the following numbers*:—

Superphosphate	100
Raw guano	30
Bone meal	10
Coprolite powder	9
Thomas slag, finest	61
,, ,, fine	58
,, ,, coarse powder ...	13

Field experiments with manures are highly valued in agriculture and undoubtedly furnish valuable, though somewhat empiric, information. In many of these trials the manures are taken at the usual trade valuation, and it is highly probable that in a large number of cases the phosphoric acid of superphosphates appears to yield better results than it really does, because of the trade custom of ignoring the insoluble phosphates present in a mineral superphosphate and only reporting that existing in the soluble form. It therefore often happens when a superphosphate containing a stated percentage of "soluble phosphates" is employed in comparison with an equal quantity of phosphates in, say, bones or basic slag, that the "super" plot gets the benefit of the insoluble phosphates in the manure, which may amount to 4 or 5%.

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* *v.* Thomas Phosphate Powder, by Prof. Wagner, Darmstadt, 1887.

CHAPTER IX.

THE CONSTITUENTS OF PLANTS.

IN the introductory chapter an account of the elements which enter into the composition of plants has been given, and in the succeeding chapters on the atmosphere, soils, and manures, the sources from which plants obtain the necessary supplies of their food have been discussed at some length. The *ultimate constituents* of plants have thus already been considered. Their *proximate constituents*, *i.e.*, the actual chemical compounds existent in the various parts of a plant, remain to be described. In this chapter a short account of the chemistry of the chief compounds which are found in most plants will be given. To some of these substances brief allusion has already been made under "Carbon" in Chap. I., p. 8.

The following is a list of the various classes into which these compounds may be conveniently divided:—

I. Carbohydrates.
II. Fats and waxes.
III. Organic acids and their salts.
IV. Essential oils and resins.
V. Inorganic salts.
VI. Nitrogenous substances.
  (i.) Albuminoids.
  (ii.) Amides.
  (iii.) Alkaloids.
VII. Chlorophyll and other colouring matters.

I.—THE CARBOHYDRATES.

An important group of compounds the members of which constitute the larger portion of the dry matter of most plants. They are neutral bodies and contain only the elements carbon, oxygen, and hydrogen, the two latter being generally present in the proportion of 16 to 2, *i.e.*, the same as in water. As a rule they contain 5 or 6, or some multiple of 5 or 6, carbon atoms, and many of them exhibit optical activity, *i.e.*, they rotate the plane of polarised light to the right (+) or to the left (−).

Many members of the group of carbohydrates have been prepared. They may be conveniently divided into the following classes:—

A. The Amyloses or Polysaccharides.—The general formula for these bodies is $(C_6H_{10}O_5)_n$. They differ from the sugars in being less soluble in water, generally non-crystalline, and incapable of reducing alkaline copper solutions. As a rule they are readily converted, by heating with dilute acids, into sugars of the glucose class.

The most important members of this class are—

Starch
Dextrin
Glycogen
Inulin
Levulin
Gums
Cellulose.

B. The Sugars.—These substances are soluble, generally crystalline, reduce alkaline copper and silver solutions, and for the most part are fermentable under the influence of yeast, yielding alcohol and carbon dioxide as the chief products.

They may be divided into the following groups:—

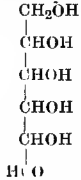
(a)* *The Glucoses or Hexo-monoses*, $C_6H_{12}O_6$:—

---

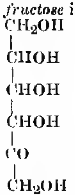
* In recent years substances possessing all the essential characters of sugars have been prepared artificially, containing from 2 to 9 atoms of carbon. These are to be regarded as belonging to the class of the mono-saccharoses or monoses, and have been distinguished by the names bioses, trioses, tetroses, pentoses, hexoses, heptoses, octoses, and nonoses

The monoses are found to combine the properties of alcohols and aldehydes, or alcohols and ketones and are sometimes divided into *aldoses* and *ketoses*. Thus—

Glucose or *dextrose* is an *aldose*. *Levulose* or *fructose* is a *ketose*.



$$\begin{array}{c} \mathrm{CH_2OH} \\ | \\ \mathrm{CHOH} \\ | \\ \mathrm{CHOH} \\ | \\ \mathrm{CHOH} \\ | \\ \mathrm{CHOH} \\ | \\ \mathrm{HCO} \end{array}$$



$$\begin{array}{c} \mathrm{CH_2OH} \\ | \\ \mathrm{CHOH} \\ | \\ \mathrm{CHOH} \\ | \\ \mathrm{CHOH} \\ | \\ \mathrm{CO} \\ | \\ \mathrm{CH_2OH} \end{array}$$

—The group $\mathrm{H}\overset{|}{\mathrm{C}}\mathrm{O}$ being characteristic of aldehydes, as $\underset{|}{\overset{|}{\mathrm{C}}}\mathrm{O}$ is of ketones.

- (i.) Glucose, dextrose, grape sugar.
- (ii.) Fructose, levulose, fruit sugar.
- (iii.) Galactose.
- (iv.) Sorbinose.
- (v.) Acrose.
- (vi.) Mannose.
- (vii.) Formose.
- (viii.) Methose.

(b) *The Saccharoses or Hexo-bioses*, $C_{12}H_{22}O_{11}$:—

- (i.) Saccharose, saccharobiose, or cane-sugar.
- (ii.) Lactose, lactobiose, or milk sugar.
- (iii.) Maltose, maltobiose, or malt sugar.
- (iv.) Melibiose.
- (v.) Trehalose, mycose.

(c) *The Hexo-trioses*, $C_{18}H_{32}O_{16}$:—

Raffinose.

Resembling the group of carbohydrates are certain other substances which occur in plants. Of these the following may be mentioned :—

(1) *The Pentoses :—*

- (i.) Arabinose, $C_5H_{10}O_5$, and araban, $(C_5H_8O_4)_n$.
- (ii.) Xylose, $C_5H_{10}O_5$, and xylan, $(C_5H_8O_4)_n$.
- (iii.) Ribose, $C_5H_{10}O_5$.
- (iv.) Rhamnose or methyl arabinose, $C_6H_{12}O_5+H_2O$.
- (v.) Fucose, $C_6H_{12}O_5$.
- (vi.) The "furfuroïds" (Cross and Bevan).

(2) *Certain Polyhydric Alcohols :—*

- (i.) Mannite or Mannitol, $C_6H_8(OH)_6$.
- (ii.) Dulcitol, $C_6H_8(OH)_6$.
- (iii.) Sorbitol, $C_6H_8(OH)_6+H_2O$.
- (iv.) Perseitol or perseite, $C_7H_{16}O_7$.

(3) *Lignone.*

(4) *Pectin substances :—*

- (i.) Pectose, $C_{23}H_{44}O_{22}$* (?).
- (ii.) Pectin, $C_{23}H_{42}O_{24}$, or $C_{32}H_{48}O_{32}$.
- (iii.) Pectic acid, $C_{23}H_{40}O_{26}$, or $C_{32}H_{44}O_{30}$.
- (iv.) Pectous acid, $C_{23}H_{42}O_{25}$.

A.—THE AMYLOSES OR POLYSACCHARIDES.

Starch or amylum, $(C_6H_{10}O_5)_n$.—This substance is very widely distributed in plants and serves as a reserve material for the nourishment of the growing portions. It exists in the form of granules, which vary greatly in size and form in different plants.

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* The composition of the pectin bodies is not well known; the above formulæ are not trustworthy.

The starch from any one source may show considerable differences in the size of its granules, but their form and general appearance is always the same and may be readily recognised under the microscope.

Of the common starches that from potatoes has the largest granules, varying from ·07 to ·03mm. in diameter, while wheat starch varies from ·045 to ·003mm., and rice starch from ·0075 to ·0050mm. in diameter.

The granule is made up of a cell wall of *starch cellulose* and an interior mass of *granulose.* So long as the cell wall is uninjured starch will not dissolve in cold water, but by bruising the cell wall, or better, by causing the granules to swell up and burst, the contents, granulose, escape and yield with the water a kind of viscid solution known as *starch paste.*

The temperature at which this swelling up of the granule occurs varies with different starches; it usually commences about 50° and is completed about 70° C.

Starch is converted by free iodine in the presence of water into a blue or violet coloured substance. Starch paste is coloured deep blue by iodine, the colour being deeper the lower the temperature; even below the boiling point of water the colour disappears entirely, but reappears on cooling The blue substance is said to have the composition $[(C_6H_{10}O_5)_4I]_4.HI$. and the presence of hydriodic acid or an iodide is said to be essential to its formation.*

Starch unites with the alkaline earths to form definite compounds which are insoluble in dilute alcohol. In the case of barium the precipitate has the composition $BaO.(C_6H_{10}O_5)_4$. A volumetric method of estimating starch has been based upon this reaction.†

When starch is heated for half an hour in glycerine to 190° it is converted into *soluble starch,* which can be precipitated from aqueous solution by the addition of alcohol. The white powder so formed is soluble in water, and according to Brown and Morris* has a molecular weight of 32,400, *i.e.*, it has the formula $(C_6H_{10}O_5)_{200}$.

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* Mylius, Ber. 20, 688; Jour. Chem. Soc. 1887, abst. 568.
† Asboth, Chem. Zeit. 11, 785; Jour. Chem. Soc. 1887, abst. 868.

Dextrin $(C_6H_{10}O_5)_{40}$ (?).—By the action of dilute acids in the cold, by the limited action of diastase (the ferment found abundantly in malt, &c.), upon starch paste, or by the action of a temperature of 210° to 280° upon dry starch, dextrin is produced, a substance easily soluble in water and giving no blue with iodine solutions.

Amylo-dextrin, with the composition $C_{12}H_{22}O_{11}.12C_6H_{10}O_5$ (*i.e.*, consisting of 1 group of maltose and 12 of dextrin), malto-dextrin, $C_{12}H_{22}O_{11}.4C_6H_{10}O_5$, and other intermediate products are formed. They have been examined and described by Brown and Morris.†

Commercial dextrin or "British gum" is obtained by heating starch to 210° or higher, or by moistening starch with a mixture of nitric and hydrochloric acids and heating it to 100° or 125° It is used as a substitute for gum arabic and probably is a complex mixture.

Dextran or fermentable gum, found in beetroots, is amorphous, soluble in water, and can be converted into dextrose by boiling with dilute acids.

Lichenin, found in Iceland moss, is soluble in hot water, but separates in flocks on cooling.

Glycogen, $(C_6H_{10}O_5)_n$, occurs in the liver and many other parts of the animal. It is a white powder, having a composition $(C_6H_{10}O_5)_2.H_2O$, and losing its water at 100°. It is soluble in water and gives a red colour with iodine. By the action of acids it is converted into dextrose, and diastase converts it into dextrin, maltose, and dextrose.

Inulin, $(C_{36}H_{62}O_{31})_2$, occurs in many plants, particularly in tubers of dahlias and Jerusalem artichokes and the roots of dandelion and chicory. It is a white powder, soluble in hot but nearly insoluble in cold water or in alcohol. It is not coloured blue by iodine, and by the action of dilute acids is converted into levulose. According to Brown and Morris,‡ its molecular weight is 1980, corresponding to the formula above given. By the action of heat, inulin forms substances similar to the dextrins.

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* J.C.S. 1889, Trans. 449.

† J.C.S. 1889, Trans. 449.

‡ J.C.S. 1889, Trans. 464.

Levulin, $(C_6H_{10}O_5)_n$, occurs associated with inulin in dahlias and artichokes. It is also found in immature grain, particularly in rye and in oak bark. It is an amorphous, deliquescent substance, yielding a mixture of dextrose and levulose by treatment with acid.

Triticin is a similar substance found in couch-grass. Other substances obtained from different sources have been described, but their individuality is not very marked.

Gums, $(C_6H_{10}O_5)_n$, are very widely distributed in plants. They are amorphous and either dissolve in water or absorb it and swell up when immersed in it. They are not coloured by iodine, and by boiling with dilute acids they yield sugars, often arabinose or xylose.

Some of these substances are employed in the arts, *e.g.*, gum arabic, the exudation from the bark of several species of acacia. This substance contains 3 or 4 % of ash (mainly lime), and as its principal constituent arabin or arabic acid, a white solid soluble in water, of highly complex constitution ($C_{89}H_{142}O_{72}$ or $C_{78}H_{120}O_{63}$[*]). Very similar bodies are found in nearly all vegetable tissue. Wood gum, the name given to the substance occurring in wood, the straw of cereals, &c., is a substance of this class. By boiling with dilute acids or alkalies, some gums yield pentose sugars, arabinose, xylose, or lyxose, $C_5H_{10}O_5$. They, therefore, belong to the class of bodies for which the name *pentosan* has been proposed, of the composition $(C_5H_8O_4)_n$. It appears[†] that the effect of boiling arabin with dilute acid is to add gradually the elements of water and to cause the splitting off of a sugar molecule, leaving a residue known as arabinosic acid, which, by further boiling, loses another sugar molecule, giving a lower acid—β-arabinosic acid—and so on, until finally an acid of the formula $C_{23}H_{38}O_{22}$ is left.

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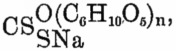
[*] O'Sullivan.

[†] O'Sullivan, Jour. Chem. Soc. 1882, 41.

$$C_{78}H_{120}O_{63}+H_2O = C_5H_{10}O_5+C_{73}H_{112}O_{59};$$
finally $C_{73}H_{112}O_{59}+13H_2O = 10C_5H_{10}O_5+C_{23}H_{38}O_{22}$.

Some gums, on boiling with dilute sulphuric acid, yield not only arabinose or xylose, as above, but galactose, $C_6H_{12}O_6$, as their main product. Hence gum is a name which includes both *pentosans* and *glucosans* (*i.e.*, polysaccharides, which yield pentose and hexose sugars).

Cellulose is the substance which constitutes the main portion of the frame-work of plants. It occurs in numerous forms, and in plants is always mixed or combined with other products of growth, from which it can usually be separated by taking advantage of its inertness and resistance to most reagents. By treating the plant tissues with chlorine, boiling with alkaline solutions, washing, treating with dilute acid, water, alcohol, and ether, a residue of nearly pure cellulose is usually obtained. Its composition corresponds to the empiric formula $C_6H_{10}O_5$. Ordinary air-dried specimens always contain 7 to 9 % of hygroscopic moisture. It is insoluble in most solvents, but can be obtained in solution by means of zinc chloride or ammoniacal copper oxide. The solubility of cellulose in these solutions is taken advantage of in the arts, the former being used in the preparation of the "carbon filament" of incandescent electric lamps, and the latter in the manufacture of "Willesden" waterproof paper. Cellulose appears to have at the same time faint acid and basic properties; it will absorb and retain either bases or acids.

By the action of caustic soda solutions (exceeding 10 % Na_2O) ordinary cotton fibre (practically cellulose) is converted into a compound which, on treatment with water, is decomposed, a molecule of water apparently taking the place of Na_2O. The properties of the fibre are changed considerably, it swells laterally or thickens with a corresponding shrinkage in length, its tensile strength is increased, and it possesses greater affinities for dyes. These facts were discovered by Mercer many years ago, and cotton fabrics so treated have lately been extensively made. They are sold as "Mercerised cotton." If cotton be treated with a solution containing 15 % of caustic soda, squeezed, and placed in a bottle with about 40 % of its weight of carbon disulphide, CS_2, a substance is produced after three or four hours which will dissolve in water on standing. This cellulose thiocarbonate,  $CS\genfrac{}{}{0pt}{}{O(C_6H_{10}O_5)_n}{SNa}$, spontaneously decomposes, especially in contact with a large amount of water, giving a jelly or coagulum. Heating also effects the coagulation. This product lends itself to many useful applications and is employed commercially under the name of "Viscose."

By the action of nitric acid, or better, a mixture of nitric and sulphuric acids, cellulose is converted into various nitro-derivatives or nitrates, some of which are of great value in the arts.

Gun-cotton is chiefly cellulose hexa-nitrate $C_{12}H_{14}(NO_3)_6O_4$, and is valued for its explosive properties. *Pyroxylin* or *collodion* is mainly tetra-nitrate, $C_{12}H_{16}(NO_3)_4O_6$, and penta-nitrate, $C_{12}H_{15}(NO_3)_5O_5$. These substances are soluble in ether and alcohol and are then known as collodion. This is employed in surgery and photography, also in the manufacture of celluloid, which is a mixture of nitrocellulose and camphor.

Parchment paper is obtained by immersing ordinary unsized paper in sulphuric acid and then washing it with water. It closely resembles true parchment in strength and apparently has the outer part of its cellulose altered into a substance known as *amyloid*. A similar change is produced by zinc chloride solution, and since amyloid is, like starch, coloured blue by iodine, a solution of iodine in concentrated zinc chloride forms a useful reagent for the identification of cellulose.

By the action of sulphuric acid cellulose is eventually converted into dextrin and dextrose.

B.—THE SUGARS.

(a) *The Glucoses, Hexo-monoses, or Hexoses*, $C_6H_{12}O_6$.

The hexoses occur widely distributed in the vegetable kingdom, being found in the free state (as in ripe fruits) or in combination with organic acids as *glucosides*.

They are produced by the *hydrolysis* (*i.e.*, the addition of the elements of water), of the di-saccharoses, polysaccharides, or of the glucosides. The hydrolysis is usually effected by unorganised ferments or by the action of hot acids. The glucoses thus may be regarded as the anhydrides of the di- and poly-saccharides.

They are generally crystallizable substances, soluble in water, possessing a sweet taste, and nearly insoluble in alcohol. They generally exhibit optical activity, *i.e.*, they rotate the plane of polarised light.

They show the reactions of alcohols and ketones or aldehydes, and possess the power, in presence of alkalies, of reducing cupric oxide to cuprous oxide. With phenyl-hydrazine, $H_2N.NH(C_6H_5)$, the hexoses yield, in presence of acetic acid, crystalline precipitates known as *osazones*.

$$C_6H_{12}O_6+3H_2N.NH.C_6H_5$$
$$=\underset{\text{Glucosazone.}}{C_6H_{10}O_4(N.NH.C_6H_5)_2}+2H_2O+NH_3+\underset{\text{Aniline.}}{NH_2.C_6H_5}$$

Many of the hexoses are capable of fermentation under the influence of yeast, *Saccharomyces cerevisiæ*, yielding alcohol and carbon dioxide as the chief products.

$$C_6H_{12}O_6 = 2C_2H_6O+2CO_2.$$

Small quantities of amyl alcohol, $C_5H_{11}OH$, glycerol, $C_3H_5(OH)_3$, and succinic acid, $C_2H_4(COOH)_2$, are also formed. Glucose, mannose, d-galactose, and d-fructose are thus affected, while sorbose, gulose, l-fructose, and the other hexoses do not ferment with yeast.

Mannose, $C_6H_{12}O_6$, is the aldehyde of mannitol or mannite, $C_6H_{14}O_6$, a sweet substance occurring in many plants, especially in the manna-ash *(Fraxinus ornus)*, the dried sap of which constitutes *manna*. The sugar is obtained by oxidising mannitol by means of platinum black. It can also be obtained from the reserve cellulose contained in many seeds by the action of dilute sulphuric acid.

Glucose, $C_6H_{12}O_6=CH_2OH.(CHOH)_4.CHO$, also called dextrose and grape sugar, occurs in many fruits, generally associated with fructose. It is formed by the hydrolysis of polysaccharides, *e.g.*, starch, dextrin, and cellulose, of cane sugar, or of glucosides.

Commercially glucose is made by boiling starch with dilute sulphuric acid. So obtained it is used in brewing and in the manufacture of jams and sweetmeats.

It crystallizes with difficulty and is much less sweet than cane sugar. It reduces copper solutions and easily undergoes fermentation.

Its compounds with lime and baryta, $C_6H_{12}O_6.CaO$ and $C_6H_{12}O_6.BaO$, are insoluble in alcohol.

Gulose, *Galactose*, *Talose*, and *Idose* are isomeric sugars. All these bodies are, like mannose and glucose, aldohexoses, *i.e.*, contain the group $\mathrm{H\overset{|}{C}O}$.

Fructose, $C_6H_{12}O_6 = CH_2OH.(CHOH)_3.CO.CH_2OH$, also called levulose and fruit sugar, occurs in most sweet fruits. It is produced, together with an equal amount of glucose, by the hydrolysis of cane sugar—

$$C_{12}H_{22}O_{11} + H_2O = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Levulose.}}{C_6H_{12}O_6}$$

Since cane sugar is dextro-rotatory and levulose more levorotatory than dextrose is dextro-rotatory, the mixture resulting from the hydrolysis of cane sugar rotates the plane of polarisation to the left. Hence the name *invert sugar* given to the mixture. Fructose also is formed by the action of hot water upon inulin.

An inactive form of fructose has been formed artificially by the action of lime or magnesia upon formaldehyde, COH_2, or of soda upon glycerose, *i.e.*, glyceryl aldehyde, $C_3H_6O_3$. The main product of this reaction has been called *Formose (i-fructose)*; in addition *a-Acrose (methose)* is produced.

Sorbinose or **Sorbose** occurs in the berries of the mountain ash, probably as sorbitol, $C_6H_{14}O_6$. It is a crystalline, very sweet substance, turned yellow by alkalies, and capable of reducing copper solutions. It is not fermentable by yeast.

(b) *The Saccharobioses, Dioses, or Di-saccharides.*

These sugars consist of two molecules of hexoses or monoses united together with the elimination of a molecule of water. They, therefore, possess the composition $C_{12}H_{22}O_{11}$. They are probably to be regarded as ethers, *i.e.*, the two hexose groups are probably connected together through an atom of oxygen. Cane sugar has no reducing power on copper salts and forms no osazone; it, therefore, probably contains no aldehyde nor ketone groups. Milk sugar and maltose yield these reactions and probably contain the aldehyde group —CHO.

The decomposition of the di-saccharides into hexoses or monoses by the addition of a molecule of water (hydrolysis) can be brought about by the action of unorganised ferments or enzymes, *e.g.*, diastase, ptyalin, invertin, &c., or by boiling with water and a little acid.

Cane Sugar, Saccharose, Saccharobiose, $C_{12}H_{22}O_{11}$, the most important sugar, occurs in many plants; in large quantities in the sugar-cane, in the maple, in beet-root, and in sorghum cane. The juice of the sugar-cane *(Saccharum officinarum)* contains from 16 to 18% of its weight of sugar. Beets contain from 7 to 16%. Cane sugar is also present in the juice of unripe maize, in many palms, in many roots, *e.g.*, turnips, mangolds, &c., in the sap of the lime, birch, &c., in the nectar of flowers, and, mixed with glucose and fructose, in many fruits.

Commercial sugar is chiefly prepared from the sugar-cane, the beet, and the sugar-maple. The properties of sugar are well known and need not be described here. It melts at 160°, and at 190° or 200° changes to a brown uncrystallizable substance known as *caramel*, used in colouring. It does not reduce copper salts. Boiled with dilute acids or by the action of certain ferments, it is converted into a mixture of glucose and levulose *(inversion)*. It combines with lime and baryta to form sparingly soluble saccharates, *e.g.*, $C_{12}H_{22}O_{11}.CaO.2H_2O$ and $C_{12}H_{22}O_{11}.3CaO$. These substances are decomposed by carbon dioxide, yielding a metallic carbonate (insoluble) and sugar. Cane sugar in plants is mainly contained in the stalks, while the hexoses occur chiefly in the fruits.

Milk Sugar, $C_{12}H_{22}O_{11}+H_2O$, will be described in Chap. XV.

Maltose, Malt Sugar, Maltobiose, $C_{12}H_{22}O_{11}+H_2O$, is formed by the action of diastase upon starch, dextrin being simultaneously produced. Maltose is a crystalline substance which undergoes fermentation under the influence of yeast, being first converted by an enzyme present in the yeast into glucose. It reduces copper solutions and in most of its properties closely resembles glucose. It is probably the form in which starch and other carbohydrates undergo translocation in plants.

The other saccharobioses are less important.

Mycose, *Trehalose*, $C_{12}H_{22}O_{11}+2H_2O$, have been found in several fungi and in ergot of rye.

Agavose, $C_{12}H_{22}O_{11}$, has been found in a Mexican plant—*Agave Americana*, from the juice of which a fermented drink called *pulque* is made. The sugar is inactive and reduces copper salts.*

Lupeose, $C_{12}H_{22}O_{11}$.—According to Schulze† lupine seeds contain a sugar of the above composition. It yields galactose and fructose by hydrolysis.

(c) *Trisaccharides, Saccharotrioses, Hexo-trioses.*

Meletriose, Raffinose, or **Melitose,** $C_{18}H_{32}O_{16}$, occurs in Australian manna *(Eucalyptus)*, in cotton seeds, and in small quantities in the juice of sugar beets, and accumulates in the molasses from which it can be prepared.

It crystallizes in needles or prisms containing three molecules of water. It is very soluble and does not reduce copper salts. It is fermentable.

The Pentoses, $C_5H_{10}O_5$.

These substances must now be included in the carbohydrates and are of considerable importance because of the common occurrence in plants of substances which readily yield them.

The most important pentoses are—

Arabinose, d-, l-, and inactive
Xylose
Ribose

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* Michaud and Tristan, Amer. Chem. Journal 14 (1893), 548.

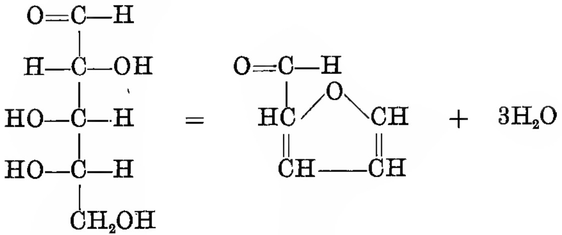
† Ber. 25, 2213; Jour. Chem. Soc. 1892, abst. 1171.

and the Methyl-Pentoses—
Fucose
Rhamnose

Arabinose, $CH_2OH.(CHOH)_3.COH$, probably never occurs as such in plants, but is obtained by hydrolysis from the *pentosans*, $(C_5H_8O_4)_n$, which occur in the gum-like constituents of many vegetable tissues. In some cases these gums yield also galactose or glucose, so that they are probably mixtures or compounds of pentosans and hexosans. Moreover the pentose obtained is sometimes arabinose, in other cases xylose. The total amount of the pentosans present in various plants has been determined by Tollens, Chalmot, Günther, Stone, and others. The following table gives some of their results:—

	%
Cherry gum	52 to 59
Gum tragacanth	32 to 38
Gum arabic	26 to 28
Wheat bran	22 to 25
Meadow hay	16 to 18
Clover hay	8 to 10
Pea straw	15 to 17
Oat straw	16 to 20
Wheat straw	26 to 27
Barley straw	22 to 25
Rye straw	22 to 25
Brewers' grains (dry) ...	27 to 31
Maize bran	38 to 43
Jute fibre	13 to 15
Wood gums (various) ...	60 to 92
Humus	1·5 to 4
Wheat (grain)	4 to 5
Maize	about 5

Arabinose is a crystalline solid, with intensely sweet taste, very soluble in hot though much less in cold water; it is insoluble in alcohol. It reduces copper solutions and forms an osazone, $C_5H_8O_3(N_2HC_6H_5)_2$, melting at 160°. Boiling hydrochloric acid converts it into furfurol—



Arabinose. Furfurol.

By the action of sodium amalgam a pentahydric alcohol, *arabite* or *arabitol*, $C_5H_{12}O_5$, is produced—a colourless, crystalline, sweet substance, resembling mannite.

Xylose, wood sugar.—This substance does not occur already formed in plants, but results from the hydrolysis of xylan, the main constituent of wood gum. The latter is very abundant in certain woods, *e.g.*, beech, and in oat straw, maize cobs, brewers' grains, &c. Xylan often occurs in plants in union with araban, hexosan, &c., as araboxylan, glucoxylan, &c. These substances upon hydrolysis yield mixtures of xylose with the other sugars.

Pure xylan, $C_5H_8O_4$, is a white porous solid nearly insoluble in cold water but soluble in hot water. Xylose crystallizes in white needles, which have a sweet taste and dissolve in water or in hot alcohol. It reduces copper salts, and on treatment with sodium amalgam yields xylite or xylitol, $C_5H_{12}O_5$.

Ribose is another isomeric pentose obtained artificially. By the action of reducing agents upon it a pentahydric alcohol—*Adonite*, $C_5H_{12}O_5$—is produced identical with that found in certain plant saps, *e.g.*, in *Adonis vernalis*.

The Methyl Pentoses.—*Fucose*, $C_5H_9(CH_3)O_5$, has been obtained from a sea-weed (*Fucus nodosis*). It is a crystalline, sweet, very soluble substance, yielding methyl furfurol on distillation with hydrochloric acid.

Rhamnose, $C_5H_9(CH_3)O_5.H_2O$, is not found in the free state in plants, but occurs very frequently in compounds analogous to the glucosides, from which dilute acids or alum solution set the sugar free. As quercitrin it has been found in many plants, *e.g.*, in sumach, hops, tea-leaves, ash, the horse-chestnut.

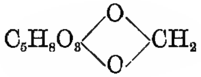
$$\underset{\text{Quercitrin.}}{C_{21}H_{20}O_{11}} + 2H_2O = \underset{\text{Rhamnose.}}{C_6H_{14}O_6} + \underset{\text{Quercetin.}}{C_{15}H_{16}O_7}.$$

Many other glucoside-like bodies have been obtained from plants, some yielding glucose as well as rhamnose.

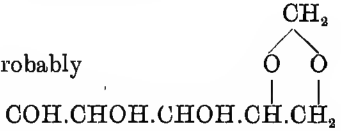
Rhamnose forms hard crystals, very soluble in water, has a sweet taste, but leaves a bitter after-taste. It loses its water of crystallization at about 105°. By reduction it forms the penta-hydric alcohol *Rhamnite* or *Rhamnitol*, $C_6H_{14}O_5$, a sweet, soluble substance.

Rhamnose, like glucose, is coloured yellow by alkalies and reduces copper salts. It is coloured violet-blue by sulphuric acid and α-naphthol.

The Furfuroids.—By this name Cross and Bevan[*] refer to the substances present in cereal straw, jute fibre, and other vegetable products, which when subjected to acid hydrolysis give furfuraldehyde. The term includes the pentoses and pentosans proper, but also another group of bodies—pentose derivatives—to which the authors just quoted ascribe the constitution—



which is probably



These bodies are capable of fermentation with yeast, yielding alcohol; in this respect they differ from the pentoses, which are apparently incapable of true alcoholic fermentation, though under certain conditions they appear to be assimilated by the yeast plant and to be destroyed.

It is probable that the pure pentoses and pentosans are not digestible (Ebstein), while these "furfuroid" bodies of the type just described appear to be so.[†] From these results it seems that the plan generally employed of determining the "total pentoses and pentosans" by distillation with dilute hydrochloric acid and precipitation of the furfuraldehyde as *osazone* gives numbers which include these furfuroid substances described above and which probably possess greater value as food stuffs than the pentoses and pentosans.

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[*] Jour. Chem. Soc. 1896, 804, 1604; 1897, 1001.

[†] Cross, Bevan, and Smith, Jour. Chem. Soc. 1897, 1003; also Cross, Bevan, and Remington, Jour. Soc. Chem. Ind. 1900.

Mannitol, Dulcitol, and **Sorbitol** are really alcohols and are related to the hexoses as described under mannose.

Perseitol is the alcohol corresponding to Manno-heptose, $C_7H_{14}O_7$.

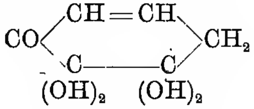
Lignose or **Lignone** (Cross and Bevan).—Lignification is the conversion of cellulose into woody fibre in the plant, a change which greatly alters the physical properties of the materials. According to Cross and Bevan this change is accompanied by a chemical change which may be empirically represented as loss of water—

$$\underset{\text{Cellulose.}}{2C_6H_{10}O_5} = \underset{\text{Ligno-cellulose.}}{C_{12}H_{18}O_9} + H_2O.$$

The ligno-cellulose, however, is, like cellulose, a highly complex substance, and probably consists of a compound of cellulose proper with lignone, an unsaturated substance containing ketone and aldehyde groups.

Ligno-cellulose therefore gives furfuraldehyde on treatment with boiling hydrochloric acid and consequently probably contains either pentosans or, more likely, furfuroids.

The ligno-celluloses are probably partially digested by the herbivora, and it is probable that the hippuric acid so characteristic of the urine of these animals is derived from the digested ligno-cellulose of their food. According to Cross and Bevan* the process of lignification in a plant is characterised by the formation of groups of the form—



$= C_6H_8O_5$

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* Cellulose, 1895, p. 77.

These groups remain in combination with the original cellulose as ligno-cellulose.

The same authors hold that the cellulose of cereal-straws, esparto grass, &c., is not normal cellulose, but oxy-cellulose. These substances contain more oxygen than cellulose, and probably CO groups. They yield furfurol on treatment with hydrochloric acid and give a characteristic rose-red colour on treatment with solutions of aniline salts. The name *hemicellulose* has been proposed for another class of cellulose, which occurs in many plants and which differs from ordinary cotton cellulose in being much more readily hydrolysed both by acids and by enzymes.

Pectin Substances.—This is the name given to the coagulable substances present in many fruit juices, stems, roots, &c. They are generally said to contain more oxygen in proportion to hydrogen than is present in a true carbohydrate, but according to Tromp, de Haas, and Tollens,* who analysed specimens of pectin derived from apples, cherries, rhubarb, currants, plums, and swedes, the ratio of oxygen to hydrogen does not differ materially from the number (8:1) observed in true carbohydrates. The percentage of carbon varies from 41 to 45%. Pectins by hydrolysis yield pentoses and hexoses. Tollens regards them as consisting of carbohydrates in union with acids.

Pectose is the parent member of the group; it occurs associated, or perhaps combined, with the cellulose as *pecto-cellulose*, and is insoluble. It is particularly abundant in unripe fruits.

Pectin, a product of the hydrolysis of pectose, is soluble in water and yields solutions which readily gelatinise. It is produced during the ripening of fruits, &c., hydrolysis being brought about either by the vegetable acids present or by an enzyme known as *pectase*.

By further hydrolysis, effected by boiling water or alkalies, *metapectin*, *parapectic acid*, and *pectic acid* are produced. The exact composition of these substances has not been determined, the analyses of the earlier investigators having been called in question by later observers (Tollens, &c.).

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* Annalen 1895, *286*, 278.

II.—THE FATS AND WAXES.

The constitution of the fats has already been briefly described (p. 11). They are glyceryl salts of the fatty acids. The true fatty acids are members of a series of which formic acid, $H.COOH$, is the first member, acetic acid, $CH_3.COOH$, the second, propionic acid, $C_2H_5.COOH$, the third, and so on, each member differing from its predecessor by CH_2. The general formula for a fatty acid would therefore be $C_nH_{2n+1}.COOH$ and its structure would be represented most simply and generally by $H—(CH_2)_n—COOH$.

Such acids are *saturated, i.e.*, cannot combine with other chemical elements or radicals by addition. Included under the title "fatty acids" and occurring in many vegetable fats are acids of a different type, *e.g.*, crotonic acid, $C_3H_5.COOH = CH_2{:}CH.CH_2.COOH$, a member of a series possessing the general formula $C_nH_{2n-1}.COOH$ and characterised by containing some doubly linked carbon atoms. In such cases the acids are said to be *unsaturated*, because under suitable conditions they can combine with hydrogen or other element, the double linkage between the carbon atoms being replaced by the usual single linkage. The fatty acids can thus be divided into two great divisions—the saturated and the unsaturated acids.

The following are a few of the more important fatty acids:—

SATURATED ACIDS.

(*a*) *Acetic or stearic acid series.*—General formula = $C_nH_{2n+1}.COOH$:—

(1) Formic acid, $H.COOH$, occurs in nettles, ants, &c.
(2) Acetic acid, $CH_3.COOH$, ,, vinegar, &c.
(3) Butyric acid, $C_3H_7.COOH$, ,, butter.
(4) Capric acid, $C_9H_{19}.COOH$, ,, butter and in cocoa-nut oil.
(5) Myristic acid, $C_{13}H_{27}.COOH$, ,, cocoa-nut oil and in spermaceti.
(6) Palmitic acid, $C_{15}H_{31}.COOH$, ,, palm oil.
(7) Stearic acid, $C_{17}H_{35}.COOH$, ,, tallow and many oils.

UNSATURATED ACIDS.

(β) *Oleic acid series.*—General formula $= C_nH_{2n-1}.COOH$:—
(1) Crotonic acid, $C_3H_5.COOH$, occurs in croton oil.
(2) Oleic acid, $C_{17}H_{33}.COOH$, ,, olive & other oils.
(3) Brassic acid, $C_{21}H_{41}.COOH$, ,, rape or colza oil.
(4) Ricinoleic acid, $C_{17}H_{32}(OH).COOH$, occurs in castor oil.

(γ) *Linoleic acid series.*—General formula $= C_nH_{2n-3}.COOH$:—
(1) Linoleic acid, $C_{17}H_{31}.COOH$, occurs in linseed and other "drying" oils.

(δ) *Propiolic acid series.*—General formula $= C_nH_{2n-5}.COOH$:—
(1) Linolenic acid, $C_{17}H_{29}.COOH$, occurs in linseed and other drying oils.

The essential difference between the saturated and unsaturated fatty acids lies in their susceptibility to the action of external agencies. The saturated compounds have no power to combine additively with oxygen, chlorine, &c., while the unsaturated compounds in many instances easily unite with these elements. The readiness with which the unsaturated fatty acids absorb oxygen and the amount which they can absorb both increase with the number of doubly linked carbon atoms contained in a molecule. Thus linolenic acid, $C_{17}H_{29}.COOH$, oxidises more readily and to a greater extent than oleic acid, $C_{17}H_{33}.COOH$. As the oxidation products are solid or stiff, viscid substances, oils containing much of these unsaturated acids are known as *drying oils;* while oils containing chiefly saturated fatty acids or acids containing only one pair of doubly linked carbon atoms, *e.g.*, oleic acid, are known as *non-drying* oils. The former are used in the arts in the manufacture of oil-cloth, linoleum, paints, &c., the latter for lubrication, &c.

Glyceryl, $C_3H_5''' = -CH_2.\overset{|}{C}H.CH_2-$ is not known in the free state, but its hydroxide, $C_3H_5(OH)_3$, is the well-known substance *glycerine*, or, as it is systematically called, *glycerol.*

Glycerol, $C_3H_5(OH)_3$, is a colourless, viscid liquid of sweetish taste. It has a specific gravity of 1·27 and mixes with water in all proportions. It is hygroscopic, and articles smeared with glycerine are kept moist both because of its non-volatility and also because it absorbs water from the air.

Glycerol is made from oils or fats by a process which shows clearly the constitution of these substances.

The oil or fat is boiled with caustic soda solution, when decomposition occurs, the sodium of the alkali taking the place of the glyceryl group, the latter uniting with the —OH of the sodium hydrate. A sodium salt of the fatty acid and glycerol are thus produced, and being soluble, remain mixed in solution. In order to separate them the sodium salts are precipitated by the addition of common salt, in a solution of which they are insoluble. The sodium salts rise to the surface and on cooling form a solid cake, constituting *soap*.

From the solution below, the glycerine can be recovered by evaporation and distillation *in vacuo*. Taking olive oil, which consists mainly of glyceryl oleate, $C_3H_5(C_{18}H_{32}O_2)_3$, as example, the reaction may be thus expressed:—

$$\underset{\text{Glyceryl oleate.}}{C_3H_5(C_{18}H_{33}O_2)_3} + \underset{\text{Sodium hydrate.}}{3NaOH} = \underset{\text{Sodium oleate.}}{3NaC_{18}H_{33}O_2} + \underset{\text{Glycerol.}}{C_3H_5(OH)_3}$$

Glycerine is also prepared by the hydrolysis of fats by means of superheated steam. Again taking olive oil as example, the reaction would be—

$$\underset{\text{Glyceryl oleate.}}{C_3H_5(C_{18}H_{33}O_2)_3} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Oleic acid.}}{3HC_{18}H_{33}O_2} + \underset{\text{Glycerol.}}{C_3H_5(OH)_3}$$

Although in the above example olive oil has been assumed to be glyceryl oleate, it must be clearly understood that this is not true and that all the oils are mixtures of the glyceryl salts of several fatty acids Thus in linseed oil, glyceryl compounds of linolenic and isolinolenic, linoleic, oleic, stearic, and palmitic acids have been found. It is not definitely known whether in the oils these substances are mixed or whether they are chemically combined, *e.g.*, whether, say, the first three compounds are present as such, *i.e.*, as—

$$C_3H_5(C_{18}H_{29}O_2)_3,\ C_3H_5(C_{18}H_{31}O_2)_3,\ \text{and}\ C_3H_5(C_{18}H_{33}O_2)_3,$$

or whether they may be present as $C_3H_5\left\{\begin{matrix} C_{18}H_{29}O_2 \\ C_{18}H_{31}O_2 \\ C_{18}H_{33}O_2 \end{matrix}\right.$

In plants, the oils are chiefly found in the seed or fruit, though small quantities are contained in the straw and roots.

Some seeds are valued chiefly for the oil which they yield, *e.g.*, rape, cotton-seed, linseed, castor, &c. There are three chief methods employed in the extraction of oil:—

(1) Pressure; the most generally employed.
(2) Extraction by volatile solvents.
(3) Boiling the bruised seed or fruit with water.

(1) *By pressure.*—By the first method the seeds are cleaned, often deprived of their husks or shells ("decorticated"), crushed, and ground, often heated and moistened, and then subjected to intense pressure in hydraulic presses. The crushed seeds are placed either in horsehair bags or in moulds and are pressed, first at the ordinary temperature, whereby "cold drawn oil" is obtained, and then after heating "hot drawn oil" is extracted. The oil obtained is refined by heating it to a temperature of about 160° C., in order to coagulate albuminoid matter, and sometimes by treatment with a little sulphuric acid. The residue left in the press constitutes "oil-cake" and usually contains from 6 to 15% of oil.

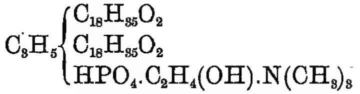
It is used for feeding or manurial purposes, since in addition to the oil it contains the albuminoid and mineral matter present in the seed.

(2) *In extraction by solvents* the crushed seeds (in bags or cages) are treated with solvents, such as petroleum naphtha or carbon disulphide, in such a way that the fresh seeds are treated first with the solvent already highly charged with oil, while the fresh solvent comes first into contact with the seeds, which are almost deprived of oil. In this way a much more complete exhaustion of the seed is obtained, leaving a residue almost devoid of oil, and therefore of much less value as a feeding stuff than the usual oil-cake.

(3) *Extraction by boiling with water* is sometimes used in the extraction of castor oil (mainly by the natives of the countries where the seed is grown) and of olive oil. The oil in such cases is merely skimmed off the top of the water.

The Waxes are substances probably occurring in small quantities in many plants. They are generally analogous to the fats in composition, except that instead of the trivalent glyceryl group they contain monovalent groups; they therefore yield monovalent alcohols on treatment with alkalies. The alcohols obtained in this way are usually complex bodies containing a large number of carbon atoms, *e.g.*, ceryl alcohol, $C_{27}H_{56}O$.(?). The waxes are solids melting below 100°, non-volatile, and insoluble in water, but soluble in ether.

Possessing a structure in some respects similar to the fats is a substance, *Lecithin*, found in many seeds, *e.g.*, beans and peas, and in fungi. This substance, of which probably several varieties occur, has a constitution which may be typified by the following formula:—



$$C_3H_5\begin{cases} C_{18}H_{35}O_2 \\ C_{18}H_{35}O_2 \\ HPO_4.C_2H_4(OH).N(CH_3)_3 \end{cases}$$

—which may be regarded as the distearyl glycerophosphate of the base, choline, $C_2H_4(OH).N(CH_3)_3.OH$.

Phytosterol, $C_{26}H_{43}OH$, which closely resembles cholesterol found in animals, occurs in the seeds of peas, beans, and almonds, in wheat, maize, and in many vegetable oils. It is a solid crystalline substance melting at 133° and soluble in hot alcohol, in ether, carbon disulphide, or chloroform. It is volatile. Its constitution is not understood, but it probably is a monacid alcohol.

III.—THE ORGANIC ACIDS AND THEIR SALTS.

A large number of organic acids have been detected in various vegetable products, occurring generally as potassium, sodium, or calcium salts, though sometimes in the free state or in combination with organic bases. Numerous acids have been detected in various vegetables; only a few typical ones can be considered here. The organic acids are characterised by containing one or more "carboxyl" groups, *i.e.*, .COOH.

The following may be taken as examples:—

Formic acid, H.COOH.
Oxalic acid, COOH.COOH.
Tartaric acid, COOH.CH(OH).CH(OH).COOH.
Malic acid, COOH.CH(OH).CH_2.COOH.
Citric acid, CH_2(COOH).C(OH)(COOH).CH_2(COOH).
Succinic acid, CH_2(COOH).CH_2(COOH).
Fumaric acid, CH(COOH):CH(COOH).

For the properties, methods of preparation, and constitution of these acids the reader is referred to any modern text-book on organic chemistry. The free acids themselves often occur in plants, particularly in fruits, *e.g.*, malic acid, occurring in apples, mountain-ash berries, gooseberries, red currants, blackberries, and sour or morella cherries.

In other cases, acid potassium or calcium salts are the cause of the acidity, *e.g.*, potassium hydrogen tartrate in grapes, acid potassium malate in sweet cherries. In many fruits several organic acids or their salts occur in association, *e.g.*, gooseberries, currants, and cherries contain both malic and citric acids, while mountain-ash berries and tamarinds contain malic, citric, and tartaric acids.

Oxalates of potassium and, particularly, of calcium are extremely widely distributed in the vegetable kingdom, the latter occurring often in the solid, crystalline state in the cells of plants. The crystals of the calcium salt have the composition $CaC_2O_4.3H_2O$ and are soluble in saccharine solutions. Acid potassium oxalates, KHC_2O_4 and $KHC_2O_4+H_2C_2O_4$, occur in solution in the sap of certain plants, *e.g.*, sorrel, rhubarb, &c.

Tannic acid or tannin is very abundantly distributed in the vegetable kingdom. It varies in composition and properties according to its origin.

Tannin was formerly looked upon as a glucoside, but the tannic acid, its chief constituent, is now looked upon as an anhydro-acid.[*] Gallo-tannic acid, for example, is said to have the constitution $C_6H_2(OH)_3.CO.O.C_6H_2(OH)_2.COOH$.

It is hydrolysed by dilute acids or by ferments, with the production of gallic acid, $C_6H_2(OH)_3.COOH$.

The natural tannins, however, are usually associated or combined with glucosides, and on hydrolysis yield glucose in addition to gallic acid.

Tannin is present in almost all plants, occurring in the bark, leaves, root, or fruit. Its origin and function in the plant are much debated questions. By some investigators it is thought to be formed by chlorophyll from carbon dioxide and water, and in many ways to resemble starch in its relationship to the plant. The tannins possess a strongly astringent taste, give intense blue- or green-black colours with ferric chloride solution, and possess the power of converting gelatin into an insoluble substance (leather). They tend to absorb oxygen, especially in presence of alkalies, giving a dark brown colouration.

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[*] Schiff Ann. 170, 43.

The nature of the acids present in the root hairs of plants does not appear to have been much investigated. Probably a number of acids are present in most cases, the predominating one varying with the species of plant. Dyer* has investigated the amount of acidity of the water contained in the root hairs of a large number of plants. He expresses his results in terms of hydrogen and in the equivalent of citric acid. He found, as is to be expected, considerable variations, but the average of about 100 different plants gave—

As hydrogen	...	·013 per 100 of water.
As citric acid	...	·910 ,, ,,

IV.—ESSENTIAL OILS AND RESINS.

These are excretions or secretions of plants, sometimes normal, sometimes as the result of injury or disease. To them the characteristic odours of certain plants are due.

The essential oils and resins often occur associated in the plant, and the latter may be regarded as products of oxidation of the former.

The essential oils may be divided into two great classes :—

1. Hydrocarbons or Terpenes.
2. Substances containing, in addition to carbon and hydrogen, other elements, *e.g.*, (i.) oxygen, (ii.) sulphur.

1. The Terpenes are again subdivided into—

(i.) Hemiterpenes, C_5H_8.—Unsaturated compounds of the valerylene series, *isoprene*, a product obtained from crude india-rubber, being the best known.

(ii.) Terpenes proper, $C_{10}H_{16}$.—The most important class.

(iii.) Poly-terpenes, $(C_5H_8)_n$.—Colophene and caoutchouc belong to this class. The sesqui-terpenes, $C_{15}H_{24}$, occur frequently in essential oils.

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* Jour. Chem. Soc. 1894, 115.

The terpenes proper are a large class; they are mobile liquids boiling between 156° and 176°. One member, camphene, is a solid obtained artificially from camphor and pinene. Most terpenes are optically active, possess characteristic though very varied odours, are insoluble in water, but dissolve readily in ether or alcohol.

By strong sulphuric acid they are converted into resinous polymers. Strong nitric acid oxidises them with inflammation. Many of them absorb oxygen from the air, forming resinous products. They all greedily absorb chlorine, bromine, or iodine.

Varieties of terpenes form the main portion of the oils of turpentine, orange, lemon, bergamot, dill, fir-needles, cummin, elemi, fennel, eucalyptus, &c.

2. (i.) **Oxygenated Essential Oils.**—Representatives of the groups—alcohols, aldehydes, ketones, phenols, and esters are found in this class. They are usually present in the oil in admixture either with one another or with a terpene. Many members of this group are known. We may mention a few typical ones :—

Alcohols.—Borneol, $C_{10}H_{17}OH$; menthol, $C_{10}H_{19}OH$. The latter occurs in oil of peppermint *(Mentha piperita).* It is a crystalline substance melting at 42° and boiling at 213°. Its acetate is also present in peppermint oil.

Esters.—Acetates and other salts of amyl and other radicals are sometimes found. Also linalyl acetate, $C_{10}H_{17}.C_2H_3O_2$, in oils of lavender and bergamot.

Aldehydes.—Oils of cinnamon and cassia contain cinnamic aldehyde, $C_6H_5.CH{:}CH.CHO$; oil of bitter almonds, benzoic aldehyde, $C_6H_5.CHO$.

Ketones.—Camphor, $C_{10}H_{16}O$, is probably a ketone. Its constitution has given rise to much discussion. According to Bredt,* it has the following formula :—

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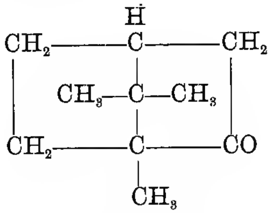
* Ann. 289, 15; J.C.S. 1894, abst. i. 141.



Aschan* has, quite recently, proved the correctness of this formula.

Camphor is obtained by distilling, in steam, the wood and bark of *Laurus camphora.* It is a colourless crystalline solid, melting at 175° and boiling at 204°. It is produced by the oxidation of some terpenes.

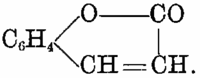
Phenols.—Thymol, $C_6H_3\underset{(1)}{(CH_3)}.\underset{(4)}{(C_3H_7)}.\underset{(3)}{OH}$, in oil of thyme.

Eugenol, $C_6H_3\underset{(1)}{(C_3H_5)}\underset{(3)}{(OCH_3)}.\underset{(4)}{OH}$, in oil of cloves.

Carvacrol, $C_6H_3\underset{(1)}{(CH_3)}\underset{(4)}{(C_3H_7)}.\underset{(2)}{OH}$, in oil of hops.

Thymol, which may be taken as typical of the group, is a crystalline body melting at 50° and boiling at 230°. It is possessed of antiseptic properties and in solution in alcohol is sometimes used in veterinary medicine as a vermifuge.

Among other oxygen-containing bodies of this class may be mentioned *coumarin*, the anhydride of ortho-hydroxycinnamic acid. It has the constitution



$C_6H_4\begin{cases} O-CO \\ CH=CH \end{cases}$.

This substance occurs in woodruff, hawthorn, and other plants.

2. (ii.) **Essential Oils containing Sulphur.**—

Oil of mustard—allyl isothiocyanate, $C_3H_5.N:C:S$.

Oil of garlic—allyl sulphide, $(C_3H_5)_2S$.

The latter is present in onions, leeks, cress, radishes, &c.

Many of the substances belonging to the last two classes are not present as such in the plant, but in union with glucose and other substances as the compounds known as glucosides; *e.g.*, almonds do not contain any benzaldehyde but *amygdaline*, $C_{20}H_{27}NO_{11}$, which in presence of water and under the action of an enzyme, *emulsin*, splits up into benzaldehyde, hydrocyanic acid, and glucose—

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* Ann. 316, 196; Jour. Chem. Soc. 1901, abst. i. 477.

$$C_{20}H_{27}NO_{11}+2H_2O=C_6H_5CHO+HCN+2C_6H_{12}O_6.$$

Similarly, allyl-isothiocyanate is not present as such in mustard seeds, but as a compound, potassium myronate, $KC_{10}H_{18}NS_2O_{10}$. This, under the action of an enzyme, *myrosin*, is split up as follows:—

$$KC_{10}H_{18}NS_2O_{10}=C_3H_5NCS+KHSO_4+C_6H_{12}O_6.$$

The Resins are now regarded as the products of the oxidation of terpenes rather than the mother substances from which terpenes are derived. They have no uniformity of constitution as is the case with the fats, but present wide differences in chemical character. They may be divided into—

1. *The Balsams*, which consist of resinous substances associated with terpenes. Canada balsam, obtained from *Pinus balsama* of South America, and crude turpentine or Venice turpentine, from many pines, are good examples.

Crude turpentine consists of ordinary rosin or colophony dissolved in turpentine oil. Rosin consists mainly of sylvinic acid, $C_{20}H_{30}O_2$,* a monobasic acid, whose sodium salt is used in the manufacture of cheap soaps.

2. *The Solid* or *Hard Resins.*—These are amorphous substances of vitreous character, which contain very little terpene. They consist chiefly of esters, alcohols, anhydrides, and acids of the aromatic series, generally of very complex character. In addition there are present certain substances which are neither hydrocarbons, esters, alcohols, anhydrides, nor acids, and which are called *resenes*. Many different bodies of this class have been isolated and analysed, but their constitution is not known, *e.g.*, from copal a substance $C_{25}H_{38}O_4$, from dragon's blood $C_{20}H_{40}O_4$. Many other substances of complicated character have been obtained from the hard resins.

To the class of hard resins belong many substances of great importance in varnish making, &c., *e.g.*, copal, dammar, elemi, sandarach, amber, &c.

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* Fahrion, Zeit. für angen. Chemie 1901, Dec. 3rd.

3. *The Gum Resins.*—These are mixtures of gums and resins, and some are of value in the arts, *e.g.*, ammoniacum, asafœtida, gamboge, myrrh, scammonium, &c.

V.—THE INORGANIC SALTS.

In the introductory chapter a list of the elements essential to plant life was given. It now remains to discuss what is known of the functions of the inorganic elements in the nutrition of plants.

Sulphur is a constituent of proteids and therefore may be said, in a measure, to be present in the organic portions of a plant. It is left in the ash chiefly as sulphate, though, as the author has observed, sometimes as sulphide. The presence of sulphates in solution in the sap can generally be detected.

Phosphorus occurs in plant ashes as phosphates, and in that form it is absorbed from the soil. In the living plant, however, it undoubtedly exists partially as organic compounds, *e.g.*, as lecithin (*v.* p. 206), and it seems to move in the plants in company with the proteids.

Silicon is probably taken into the plant as alkaline silicates. It is always found in the ash, sometimes in large quantities, as silica, SiO_2, or silicates. Indeed in many plants, *e.g.*, the cereals and grasses, large deposits of silica occur in the outer walls of the stems and leaves; but it appears that the plant derives little benefit by this and can thrive vigorously without siliceous food.

Chlorine occurs in all plants, but it cannot be proved to be essential, except perhaps in buckwheat and mangolds. Its presence seems to aid in the hydrolysis of starch.

Potassium is absorbed as various soluble salts and apparently exists in the plant in combination with organic acids, though some saps contain the nitrate, chloride, and sulphate. It is always most abundant in the parts of the plant where assimilation is most active, *i.e.*, leaves and twigs. It seems to be absolutely indispensable for the production of starch, sugar, &c., but what part it plays in their production is not known.

Calcium seems to aid in the conversion of starch into sugar. It probably exists in combination with organic acids; indeed crystals of calcium oxalate or carbonate are often found in the cells. One of its functions may be to combine with, and render harmless, the vegetable acids formed in the plant. It is found chiefly in the leaves.

Magnesium is fairly uniformly distributed; little is known of its functions.

Iron is usually present only in small proportion, but it is quite indispensable. Plants deprived of iron are unable to produce chlorophyll.

Sodium, though always present in the ash, does not appear to be essential to the vital processes. It cannot fulfil the functions of potassium.

The metals mentioned above, in addition to the special functions in connection with assimilation and other processes, act also an important part as carriers of nitric acid; when the nitrogen is elaborated into proteids, the metals unite with organic acids, which yield carbonates on ignition.* It was found that the richer a plant was in nitrogen the larger was the amount of bases left as carbonate in the ash.

VI.—NITROGENOUS SUBSTANCES.

(i.) **Albuminoids.**—This word is used in different senses by different writers; by some it is employed as synonymous with *proteid*, by others as the name of a small class of nitrogenous substances, differing from the true *albumens* (*e.g.*, gelatin and mucin). Using the term *proteid* as the generic name for the large group which may be called "Albuminous substances," it becomes difficult to define the exact meaning of the word. They are of highly complex constitution, generally non-crystallizable, and contain carbon, hydogen, oxygen, nitrogen, and sulphur. They occur in all living matter, being essential constituents of protoplasm.

The ultimate composition of proteids varies between the folowing limits (Hoppe-Seyler):—

	Carbon.	Hydrogen.	Nitrogen.	Sulphur.	Oxygen.
From	51·5	6·9	15·2	0·3	20·9
to	54·5	7·3	17·0	2·0	23·5

In vegetable tissues certain crystallizable proteids have been detected,† especially in the aleurone grains (*e.g.*, of castor-oil seeds).

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* Lawes and Gilbert, Phil. Trans. 192 (1900), 207.

† Hartig, 1885; Vines.

According to Halliburton* the vegetable proteids may be classified as follows :—

(a) *Vegetable albumens*, which are soluble in water and coagulate at 70°. These have been isolated from rye, wheat, potatoes, and other plants.

(b) *Vegetable globulins*, insoluble in water, soluble in saline solutions ; coagulate from 55° to 75°. The crystallizable proteid just alluded to (vitellin) is a globulin. An analysis of this substance gave the following numbers :—

Carbon.	Hydrogen.	Nitrogen.	Sulphur.	Oxygen.
52·43	7·12	18·10	0·55	21·80

(c) *Vegetable albuminates.*—Of these, legumin or vegetable casein is the most important. It is found in peas, vetches, beans, and lentils. It is soluble in water and yields on analysis :—

Carbon.	Hydrogen.	Nitrogen.	Sulphur.	Oxygen.
51·48	7·02	16·77	0·40	24·32

A similar substance obtained from almonds and lupines contains more nitrogen. Hoppe-Seyler states that the albuminates are not present in the plants, but are formed by the action of the alkali used in extracting the proteids.

(d) *The vegetable proteoses.*—These substances are intermediate in the formation of peptones from proteids. They differ very slightly from the peptones, being, like them, soluble and slightly diffusible. They are precipitated by nitric acid, but soluble in excess. They are common in aleurone grains.

(e) *Vegetable peptones.*—These are very soluble in water and diffusible ; they are precipitated by tannin or by absolute alcohol. Peptones do not exist in plants except transiently, being probably formed by the action of ferments upon the proteids, enabling these bodies to pass, by diffusion, to the growing portions of the organism.

(f) *Insoluble vegetable proteids.*—The most important member of this group is gluten, a tenacious, tasteless, brownish grey substance, soluble in strong acids or alkalies. It consists of two substances, one soluble in alcohol, which has been called "gliadin" or "vegetable gelatin," to which the stickiness of gluten is due, and another portion, insoluble in alcohol, which has received the name "vegetable fibrin." According to Martin gluten is not present in flour, but is produced by a ferment from other proteids during the treatment with water.

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* Watts's Dict. of Chem., Vol. IV., p. 336.

Good wheat flour contains 10 or 11% of gluten, the poorer varieties 8 to 10%. Barley, oat, and rye flours contain very little of the gliadin, their gluten consisting mainly of vegetable fibrin; hence they do not yield such sticky paste nor such spongy bread as does wheat flour.

The complex character of albumen may be gathered from the various formulæ which have been proposed as most nearly representing its composition, thus:—Lieberkühn proposed $C_{72}H_{121}N_{18}O_{22}S$, Schützenberger $C_{240}H_{392}N_{65}O_{75}S_{3}$, and Harnack $C_{204}H_{322}N_{52}O_{66}S_{2}$.

Proteids are all optically active, being lævo-rotatory. They are precipitated by acids and potassium ferrocyanide, by basic lead acetate, by mercuric chloride, by copper sulphate, by saturation of the liquid with ammonium sulphate or magnesium sulphate, or by alcohol.

The following are general qualitative tests for proteids:—

1. Heated with strong nitric acid they yield a yellow colouration which becomes orange on the addition of alkali (xantho-proteic reaction).
2. Millon's reagent (an acid solution of nitrate of mercury) gives a precipitate which turns red on heating.
3. With excess of strong sodium hydrate solution and a small quantity of copper sulphate a violet colour is obtained, becoming deeper on warming.
4. Adamkiewicz's reaction. The proteid is dissolved in glacial acetic acid and strong sulphuric acid is added, when a violet colour is produced. It has lately been shown* that the acetic acid only produces this reaction if it contains as an impurity, glyoxylic acid, HCO.COOH, and

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* Hopkins and Cole, Proc. Roy. Soc. 1901, 21.

that a better method of performing the test is to reduce oxalic acid by means of a little sodium amalgam, thereby forming glyoxylic acid, add a few drops of this solution to that of the proteid, and then sulphuric acid.

The usual method of estimating proteids in analysis is by determining the amount of nitrogen present, and then assuming that this nitrogen constitutes about 16% of the weight of the albuminoids. The percentage of nitrogen found is therefore multiplied by 6·25, and the product is given as the percentage of albuminoids. This only gives approximate values, since all proteids do not contain exactly 16% of N. The following table gives the percentage of nitrogen found in various proteids and the factor which, multiplied by the percentage of nitrogen found, will give the amount of albuminoid present*:—

Substance.	Percentage of nitrogen.	Factor.
Mucin ...	13·80 to 14·13	7·25 to 7·08
Albuminates ...	13·87	7·21
Oat proteids ...	15·85	6·31
Egg albumen ...	15·71 to 17·85	6·37 to 5·60
Maize proteids ...	16·06	6·22
Casein ...	15·41 to 16·29	6·49 to 6·13
Serum albumen ...	15·96	6·27
Peptones ...	16·66 to 17·13	6·00 to 5·84
Wheat proteids ...	16·80 to 18·39	5·95 to 5·44
Flax seed proteids	17·70 to 18·78	5·65 to 5·33

(ii.) **Amides.**—These substances have already been defined as organic acids in which the —OH groups have been replaced by $—NH_2$ groups. In some cases, *e.g.*, in the case of monobasic acids, the product is a true amide, while in others, *e.g.*, when the acid is polybasic, there may be a true amide, in which all the acidic —OH groups are replaced by an equal number of $—NH_2$ groups, or an amic acid may be formed. For example, from carbonic acid, $CO(OH)_2$, there are obtainable—

(1) Carbamide (urea), $CO(NH_2)_2$, *i.e.*, $NH_2.CO.NH_2$, and
(2) Carbamic acid, $NH_2.CO.OH$.

Under the name amides are included compounds of both types.

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* Wiley, Agric. Analysis, Vol. III., p. 445.

The amides are widely distributed in the vegetable kingdom, being found in especially large quantities in immature plants.

The most important bodies classed as amides occurring in plants are :—

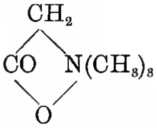
1. *Asparagine*, which is really amido-succinamic acid, $C_2H_3(NH_2)\left\{\begin{matrix}CO.NH_2\\CO.OH,\end{matrix}\right.$ is found in the juice of the asparagus, in many fruits, roots, and tubers, in the young shoots of vetches, beans, peas, &c. Asparagine crystallizes with one molecule of water in prisms. It has a cooling, unpleasant taste, and is soluble in about 80 parts of water. By boiling with alkalies or other bases aspartic acid or amido-succinic acid, $C_2H_3(NH_2)(COOH)_2$, is formed, with evolution of ammonia.

Dilute hydrochloric acid produces the same acid and ammonium chloride, the nitrogen of the amide ($—CONH_2$) group being converted into ammonia. This is a general reaction with amides.

2. *Glutamine*, amido-glutamic acid, $NH_2.CO.C_3H_5(NH_2).COOH$, is found in beetroot, the shoots of the vetch, and in the pumpkin. It crystallizes in slender white needles, which contain no water of crystallization. It is very soluble in hot water, but insoluble in absolute alcohol.

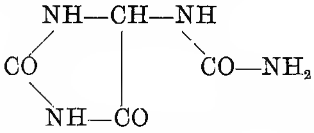
3. *Choline*, hydroxyethyl-trimethyl-ammonium hydroxide, $C_2H_4(OH).N(CH_3)_3.OH$, occurs in cotton seed, in beets, in hops, and in many other plants. It is a syrupy liquid with a strong alkaline reaction. It appears to possess poisonous properties, which are sometimes apparent when cotton seed is used as a food for very young animals. It forms a characteristic reddish yellow crystalline compound with platinum tetrachloride, $(C_5H_{14}ON)_2PtCl_6$.

4. *Betaine*, trimethlyl glycocoll, is said to have the composition—



It is found in beet juice, in mangolds, and in cotton seed. It is formed by the oxidation of choline. It crystallizes with one molecule of water.

5. *Allantoine*, $C_4H_6N_4O_3$, found principally in animal products, has been detected in certain vegetables, *e.g.*, in plane-tree leaves and in the sprouts of many young plants and in cereals. It crystallizes in prisms, soluble in hot water and in alcohol, and has a neutral reaction. It is di-ureide of glyoxylic acid and has the constitution—



6. *Leucine*,* amido-caproic acid, $CH_3.(CH_2)_3.CH(NH_2).COOH$, occurs in many animal substances, *e.g.*, the liver, spleen, pancreas, &c., and in many vegetable products, *e.g.*, vetch sprouts, the pumpkin, &c. It is also formed readily from many albuminoids by the action of sulphuric acid, ferments, or caustic potash. It is a white crystalline substance, melting at 170° and volatile without decomposition. Its solubility in water is not great and it is less soluble in alcohol. It dissolves readily in either acid or alkaline solutions.

7. *Tyrosine*, paraoxyphenyl-α-amido-propionic acid, $C_6H_4(OH).CH_2.CH(NH_2).COOH$., often accompanies leucine as a product of the action of digestive enzymes upon albuminoids. It crystallizes in fine needles and is readily soluble in hot though only sparingly in cold water; it is insoluble in ether or alcohol.

The amides play an important part in plant nutrition. Being soluble and diffusible they can readily pass from one part of the plant to another, which is not the case with the colloidal albuminoids.

The amides are apparently not capable of forming flesh in an animal, though they doubtless aid in fat formation and in heat evolution. It is evidently very important, therefore, to discriminate between amides and albuminoids in examining vegetable food stuffs. In many analyses which have been published this has not been done, and in the case of certain varieties of foods, *e.g.*, roots, the results obtained in practice do not correspond with what might be expected from the figures of such analyses. In the modern analyses a distinction between the two classes of nitrogenous ingredients of food is made, and chemical analysis and experimental feeding agree much more nearly.

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* According to Fischer (Ber. 33, 2371), leucine is α-amido-isobutyl acetic acid, $(CH_3)_2.CH.CH_2.CH(NH_2).COOH$.

Both amides and albuminoids yield their nitrogen as ammonia when treated by the Kjeldahl process (*v.* Chap. V., p. 93.), and the total nitrogen obtained by the application of this process to the food stuff is first estimated. In order to determine the amount of nitrogen present as amides either of the two following methods may be used.

1. A weighed quantity of the material is boiled for half an hour with 5% solution of hydrochloric acid or sulphuric acid. The albuminoids are not affected, but the nitrogen of the amide group is thus converted into ammonium chloride or sulphate, *e.g.*:—

$$2\,[\underset{\substack{\text{Asparagine.}\\\text{Amido-succinamic acid.}}}{CO(NH_2).C_2H_3(NH_2).COOH}] + 2H_2O + H_2SO_4$$

$$= 2\,[\underset{\substack{\text{Aspartic acid.}\\\text{Amido-succinic acid.}}}{C_2H_3(NH_2)(COOH)_2}] + (NH_4)_2SO_4$$

The solution is then exactly neutralised with sodium carbonate and distilled with magnesia, the ammonia evolved being received in standard acid. Half the nitrogen contained in asparagine is thus obtained as ammonia. It is usual to report all the amide nitrogen in terms of asparagine.

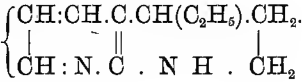
2. A weighed quantity of the food is treated with water containing freshly precipitated, well-washed copper hydroxide, filtered and washed; the amides pass into solution; a nitrogen determination by the Kjeldahl process in the residue gives a measure of the true albuminoids.

The Alkaloids.—These substances are nitrogenous bases, possessed usually of powerful therapeutic properties. They are very numerous and in constitution are generally to be regarded as derived from ammonia, NH_3, by the replacement of a part of or all the hydrogen by complex groups. With few exceptions, *e.g.*, nicotine, coniine, and sparteine, they contain oxygen. They exist in the plant probably as salts of organic acids. They are only slightly soluble in water, more so in alcohol. They are found in various parts of plants and may be extracted by digesting the finely divided material with dilute sulphuric acid, nearly neutralising the solution with alkali, boiling down, and adding alcohol, when most of the gums, mucilage, &c., are precipitated and the alkaloids remain in solution.

Some of the more important alkaloids are—

Coniine, $C_8H_{17}N$ = propyl piperidine, $C_5H_{10}(C_3H_7)N$.

Nicotine, $C_{10}H_{14}N_2$ = dipyridyl hexahydride



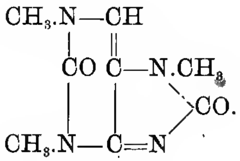
$$\left\{\begin{array}{l} CH{:}CH.C.CH(C_2H_5).CH_2. \\ \;|\qquad\quad\;\; \| \qquad\qquad\qquad\quad\; | \\ CH:N.C\ .\ N\ H\ .\ CH_2 \end{array}\right.$$

Morphine, $C_{17}H_{19}NO_3$.

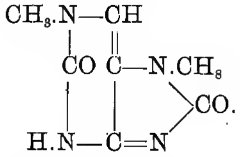
Strychnine, $C_{21}H_{22}N_2O_2$.

Quinine, $C_{20}H_{24}N_2O_2$.

Caffeine or Theine, $C_8H_{10}N_4O_2$ =
(Trimethyl xanthine)



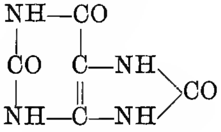
Theobromine, $C_7H_8N_4O_2$ =
(Dimethyl xanthine)



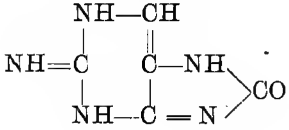
The two latter bodies, though different in constitution from the true alkaloids, are important constituents of certain plants —tea (and coffee) and cocoa; they are intimately connected in chemical constitution with xanthine, $C_5H_4N_4O_2$, found in many animal products and in certain plants; with guanine, $C_5H_5N_5O$, found in guano (p. 130); and with uric acid, $C_5H_4N_4O_3$, found in urine.

The following formulæ will illustrate these connections:—

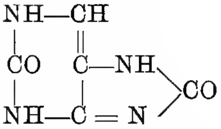
Uric acid.



Guanine.



Xanthine.

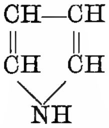


The alkaloids are as a rule poisonous and are of no value as direct foods, though their presence in food stuffs, *e.g.*, tea, &c., is of great importance.

VII.—CHLOROPHYLL.

This substance is the essential constituent of all the green-coloured portions of plants and is the medium by which the assimilation of carbon compounds from carbon dioxide and water by the aid of energy derived from light takes place. Its chemical composition and constitution are not well known, though they have been the subjects of an immense amount of research. According to Schunck and Marchlewski the chlorophyll obtained from all varieties of plants is the same. Other observers, *e.g.*, Etard, consider that many different chlorophyll-like bodies occur.

The constitution of chlorophyll resembles that of the colouring matter of blood, and both substances are probably derivatives of pyrrol, C_4H_5N[*] =



Chlorophyll is readily extracted from plants by ether, carbon disulphide, or alcohol. By the action of hydrochloric acid chlorophyll is converted into phylloxanthine, which on further treatment with acid yields phyllocyanine. These substances, as their names imply, possess a yellow and blue colour respectively.

By further action of hydrochloric acid or of alkalies phyllocyanine is converted into phyllotaonin, a crystalline body having a composition corresponding to the formula $C_{40}H_{38}N_6O_5$.[†]

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[*] Schunck and Marchlewski, J.C.S. 1896, abst. i. 574.
[†] Schunck and Marchlewski, J.C.S. 1894, abst. i. 341.

Though the presence of iron in a plant is absolutely indispensable for the formation of chlorophyll, the coloured substance itself is free from that element.

Chlorophyll and its derivatives give characteristic absorption spectra, the black bands formed in the continuous spectrum of white light which has been filtered through a solution of chlorophyll showing the particular rays which are absorbed and whose energy is utilised in the assimilative processes of the plant (*v.* next chapter).

Many other coloured or colour-yielding substances occur in plants, but their importance in reference to the life of the plant in most cases is small or not understood.

CHAPTER X.

THE PLANT.

For a description of the structure and general life-history of plants the reader will naturally turn, not to a work on agricultural chemistry, but to a treatise on botany.

Nevertheless, a brief account of the functions of the various parts and their special adaptation for carrying on the processes of life may usefully be given here.

Germination.—A seed is essentially a germ or embryo, together with a store of reserve material from which the future plant is to be formed (endosperm or cotyledons). The embryo is the only portion of the seed which is really alive, the endosperm, *e.g.*, of barley or wheat, is merely a store of food; hence it is possible to transplant the embryo from one seed to another without destroying its power of growth. The nature of the food stored in a seed varies; there is always a considerable amount of albuminoid matter and either starch or fat.

Seeds suffer little change by keeping, provided they be protected from moisture; if not already dry they lose water, and in some cases carbon dioxide, but these changes soon cease and no further loss occurs. Vitality may be retained for several years. When placed under suitable conditions seeds germinate. The most important circumstances affecting germination are—

(1) Moisture.
(2) Temperature.
(3) Access of oxygen.
(4) Removal of carbon dioxide.

Moisture is essential and acts by producing considerable swelling, accompanied by a rise of temperature.

A suitable temperature is also requisite. As a rule no germination occurs below 3° or above 49°. The limits as well as the optimum temperature vary with different seeds. The temperature of most rapid germination is usually between 25° and 33°.

During germination oxygen is actually absorbed in considerable quantity, carbon dioxide being exhaled.

The process of oxidation produces heat, and a considerable rise of temperature may be observed when many seeds germinate together (*e.g.*, in malting barley). During this slow combustion the fats and carbohydrates are consumed, but the proteid matters remain undiminished in quantity.

In germination various enzymes present in the seed commence to act (diastase, which has the power of converting starch into maltose and dextrose, is a typical one), whereby the reserve materials in the seed are converted into soluble substances capable of transportation in the sap. The embryo increases rapidly in size, sending upwards a plumule, which will eventually produce the stem, and downwards a radicle, destined to form the root. The direction of growth of the plumule and radicle is determined by gravitation, for if seeds be germinated while subjected to centrifugal force (say on a rotating wheel) the plumule grows towards and the radicle away from the centre of rotation. As soon as the plumule reaches the surface of the soil and becomes exposed to light, chlorophyll is produced in it and assimilation commences. The radicle, too, develops root-hairs and becomes capable of taking in plant food from the water of the soil.

Before describing the chemical changes which occur in plants it may render the matter clearer if a few terms which are used in physiology be explained.

Metabolism refers to all chemical changes which occur in or are produced by living matter. These are further subdivided into—

(1) *Anabolism* or constructive metabolism, including all processes in which complex compounds are built up from simpler ones by the aid of living organisms. The final stage of all anabolic processes is the formation of protoplasm. In the case of plants the most characteristic anabolic process is the synthesis of carbohydrates from

carbon dioxide and water. This is the first portion of the process of assimilation.

(2) *Katabolism* or destructive metabolism, including all chemical changes resulting in the formation of the more simple from the complex. A type of such katabolic processes is the absorption of oxygen and the liberation of carbon dioxide; this occurs most markedly in animals, but is also an essential function of plants. The process is known as respiration.

The products of metabolism are classed as *plastic products*, which can be utilised again in anabolism, and *waste products*, which cannot be again used, and which are either excreted or secreted in the insoluble form within the body of the plant or animal.

The main parts of a plant are—

(1) The roots.
(2) The stem.
(3) The leaves.
(4) The flowers and seeds.

A brief account of the functions of these will now be given :—

1. The Roots.—The radicle formed from the seed naturally grows downward, *i.e.*, in a direction towards the force of gravitation or other force acting upon it. Soon, however, it branches, and the secondary roots generally grow laterally. From these roots in turn, other branches are formed, and in the neighbourhood of the growing point of a root, root-hairs are sent out among the particles of the soil. These root-hairs have thin walls through which water can readily pass, carrying with it the dissolved matter which it may contain, provided that matter be capable of passing through the membranous walls (*i.e.*, be a crystalloid). The constituents of the sap, often including free vegetable acids, pass outwards from the root-hairs and aid in the solution of certain constituents of the soil, which, when dissolved, diffuse into the root. All the crystalloid constituents of soil-water in this way enter the root and are carried in the sap to other parts of the plant, where they are absorbed, if required, in order to build up the tissues of the plant. If not so utilised they remain in the sap and thus prevent the entrance by diffusion of additional matter of the same kind.

A few words may here be said about the phenomena of diffusion and osmotic pressure. Diffusion, as is well known, refers to the process by which a substance dissolved in a solvent, moves from the more concentrated to the less concentrated portions of the liquid. This movement is an indication of a motion which is constantly occurring in the particles of a dissolved substance, but which is only readily apparent when more of the substance moves in one direction or into a given space than moves in the other direction or out of it.

Graham in 1850 investigated the rates of diffusion of various compounds in aqueous solution and found great differences with different substances. Many crystallizable substances moved comparatively rapidly, while colloidal bodies, *e.g.*, gum, albumen, tannin, &c., moved with extreme slowness. He found, moreover, that colloidal bodies, either in solution or when thoroughly wetted with water, allowed *crystalloids* to diffuse freely, but practically stopped all diffusion of dissolved *colloids*.

The practical application of this phenomenon to the separation of crystalloids from colloids is known as *dialysis* and is usually accomplished by means of a vessel, the bottom of which is composed of animal or vegetable parchment. The mixture of the two dissolved substances is placed within this vessel, which is then floated upon pure water; the crystalloid passes through the membrane, but the colloid does not. The diffusion of the crystalloid goes on with diminishing speed until the concentration of the solution within and without the *dialyser* becomes equal. Even then, it is to be clearly understood, the action probably does not cease; but, since just as much leaves the inner vessel in a given time as enters it, the process does not readily show itself.

By repeatedly renewing the water in the outer vessel the whole of the crystalloid may be removed from the liquid within the dialyser, while the amount of colloid is not appreciably diminished.

In all cases of diffusion it is obvious that any dissolved substances move from the stronger solution to the weaker one, so that equality in concentration is approached. In many cases the attainment of this equality is facilitated by the movement of a greater quantity of the solvent from the weak to the strong solution. Certain substances when arranged as a partition between a solution and the solvent will permit of the passage of the solvent only, but not the dissolved substance. Perfect *semi-permeable membranes*, as they are termed, are not known, but a near approach to them can be made artificially by producing a precipitate of copper ferrocyanide within a porous earthenware cell. If such a cell be filled with a solution, closed, and its interior be connected with a manometer, it will, when immersed in the solvent, show the production of considerable pressure, in some cases amounting to several atmospheres. The pressure attained in any experiment will, when it has become constant, be found to vary directly with the concentration and to increase with a rise of temperature. This *osmotic pressure*, as it is termed, has been shown to be analogous to gaseous pressure and to be amenable to the laws of Boyle and Charles.

The cell walls of plants, or rather their protoplasmic linings, are probably composed of an approximately semi-permeable membrane; hence if they are surrounded with a solution of less concentration than their contents, they will receive more liquid than they will lose, and the pressure within the cell will be increased; on the other hand, if the solution outside be more concentrated than that within, more liquid will leave than will enter, and the cell will shrink. The outer part of the cell walls (cellulose) is not merely semi-permeable, but allows of free diffusion. It, however, has not much power of extension and so acts as a nearly rigid and strongly elastic envelope for the protoplasm. It is the strain set up by turgescence of the cells which is the chief cause of the rigidity and firmness of vegetable tissues in spite of their high water content. (A turnip, though so firm and hard, for example, contains far more water and less solid matter than milk or beer.)

The stems and leaves of plants owe their stiffness and erectness to the same cause—the strain produced by the elasticity of the cellulose envelopes on the one hand and the water-distended state of their protoplasmic contents on the other. When this turgescence relaxes, *e.g.*, by evaporation, the plant wilts and droops, becoming quite flaccid.

A solution within a cell composed of a semi-permeable membrane and closed by a manometer, if immersed in the pure solvent, takes in the latter until the osmotic pressure is in equilibrium with the pressure produced by the mercury column of the manometer. If more mercury be added to the manometer some of the solvent will be forced out; on the other hand, if the mercury column be shortened more solvent will enter and the volume of liquid within the cell will increase. It is found that the pressure produced by a given weight of dissolved substance per litre of solution at a given temperature is exactly equal to the pressure which would be exerted by the substance if it could exist as a gas under the same conditions as to volume and temperature. This latter, in the case of different substances, varies inversely with the molecular weight of the substance. Consequently it is found that two solutions exert an equal osmotic pressure when there are present in a given volume of the solution the same number of molecules of the dissolved substances. In the case of most metallic salts and the stronger acids in aqueous solution, this law is subject to a correction, because of the dissociation of these compounds into ions, each of which acts as a molecule.*

A living vegetable cell has been employed as a means of detecting the equality of the osmotic pressures existing in two solutions. If the cell be surrounded with a solution in which the number of molecules of dissolved substance per unit volume be greater than that in the sap within it, the water will pass through the protoplasm out of the cell, and the protoplasm will shrink from the rigid cellulose wall. This phenomenon is known as *plasmolysis* and can be observed under the microscope. With a certain strength of liquid the cell contents will be in equilibrium, *i.e.*, no water will leave or enter. Solutions of different salts have the same osmotic pressure or are *isotonic* if they are in equilibrium with the sap of the same cell.

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* *v.* p. 82.

As already stated, perfect semi-permeable membranes are not known, and all membranes that have been observed permit of a slight amount of diffusion of the dissolved matter as well as of the solvent through them.

It is therefore probable that diffusion of dissolved substances from without and the setting up of osmotic pressure within the roots are processes opposed to each other, and their simultaneous occurrence is possible only because the roots are neither truly semi-permeable membranes on the one hand, nor merely porous colloidal bodies, permitting of free diffusion, on the other.

The living protoplasm of a vegetable cell thus permits of slight diffusion of its contents outwards and of the dissolved matters present in the surrounding liquid inwards, though at the same time showing the production of internal osmotic pressure owing to the fact that the liquid within itself is more concentrated in solid matter (*i.e.*, contains more molecules of dissolved substances per unit volume) than the liquid without. In the spring, when the plant juices become richer in dissolved matter (probably owing to the activity of ferments contained in the tissues leading to the production of sugar from starch, amides from albuminoids, &c.), the osmotic pressure, aided by a rise in temperature, becomes greatly increased, and, as a consequence, the roots of the plant, taking in large quantities of water from the soil, while losing comparatively little by diffusion, set up *root pressure*, which forces the sap up into the stem and leaves.

The magnitude of this root pressure in certain plants has been measured and found to rise sometimes to three or four atmospheres.

It is through the roots, by diffusion, that the mineral matters and the nitrogen (in the form of nitrates) required by a plant are taken in and forced, largely by osmotic pressure (due mainly not to them, but to the organic constituents present in the sap), up into the stem and leaves.

The diffusion of substances in solution from one part of the plant to another is made easier and does not tend to set up osmotic pressure between different parts of the plant, because of the fact revealed by the researches of Gardiner* and others that the protoplasm is continuous from cell to cell, the continuity being maintained by fine threads passing through minute perforations in the cell walls. Through these small apertures, diffusion of dissolved matter in the protoplasm itself will take place at a rate probably far greater than is proportional to their area. The apertures, in fact, as suggested by Brown and Escombe,* play a similar part to the stomata in the leaves in promoting diffusion without interfering with the structural advantages of the cell walls.†

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* Proc. Roy. Soc. 62 (1897), 100.

2. The Stem from our present aspect may be regarded as the mere means of communication between the roots and the leaves. It, however, serves many other purposes, *e.g.*, often as a receptacle for reserve material or for excreted matters, and to some extent, when green, as an assimilative agent.

3. The Leaves are the seat of the most important chemical changes occurring in the plant. It is here that the reactions characteristic of vegetable life mainly take place—the formation of carbohydrates from carbon dioxide and water, of amides and albuminoids from the same constituents and the nitrates and sulphates taken in through the roots. They also fulfil another most important function—as a means by which the water absorbed by the root may be got rid of by evaporation. This process of *transpiration*, as it is called, takes place at a rate which depends upon several circumstances, among others upon the hygrometric state of the atmosphere round the leaf. The absorption of carbon dioxide and the evaporation of water take place mainly through the minute openings on the exterior of the leaf known as *stomata*. Each *stoma* is provided with two guard cells, by the varying turgescence of which the size of the opening can be regulated. If the guard cells become flaccid, as they tend to do by excessive loss of water by transpiration and also in the dark, they more nearly close the opening—the stoma—between them and so lessen the passage of water vapour outwards and of carbon dioxide inwards. The space below the epidermis of a leaf is surrounded by cells which contain *chlorophyll*, and it is the energy of light absorbed by this colouring substance which effects the decomposition of carbon dioxide. It is found that the assimilation of carbon dioxide is most active in just those rays of the spectrum of white light which are absorbed by a solution of chlorophyll. This is well shown in the accompanying diagram, which gives the relative assimilation by plants in different parts of the spectrum (continuous line), and also the relative absorption by a solution of chlorophyll (dotted line). It will be seen that the two curves correspond very closely*:—

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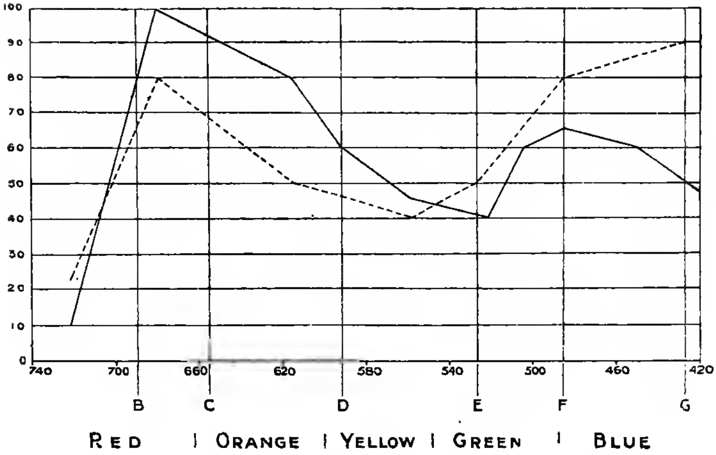
* Phil. Trans. 193 (1900), 280. † v. p. 233.



The following diagram gives the distribution of the intensities of the various rays of the solar spectrum as regards assimilation of carbon (continuous line ———), brightness as measured by the eye (broken line - - - - - -), heating effects (dotted line ....), and chemical action on silver salts (broken and dotted line —.—.—.—)†:—

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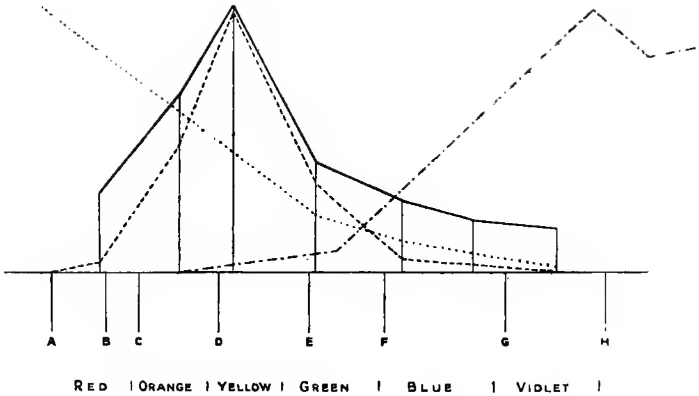
* Engelmann, Bot. Zeitung, 1884, 80.

† Sachs, Plant Physiology, p. 305.



These two diagrams do not agree as to the position of the maximum assimilation, the former placing this in the orange red, where the darkest absorption band of chorophyll actually occurs; the latter on the greenish side of the yellow, where the rays brightest to the eye occur. The former diagram is probably the more correct.

In connection with the action of light upon plants, it may be pointed out that though light of low refrangibility (*i.e.*, near the red end of the spectrum) is undoubtedly most active in promoting carbon assimilation, yet light of short wave length (*i.e.*, from the violet end of the spectrum) is of most importance in directing the motion of the leaves or of affecting the growth in length of the shoots.

With reference to our knowledge of the method by which the carbon dioxide of the atmosphere is brought into contact with the chlorophyll-containing cells, considerable advances have recently been made. Blackman in 1895* described experiments by which he proved that carbon dioxide found its way into (in assimilation) and out of (in respiration) the leaves almost exclusively by the stomata, and not—as was generally believed—by diffusion through the cuticle and epidermis. When the rate at which carbon dioxide is absorbed by a vigorously growing leaf in sunlight is taken into account, and also the very limited area of the stomatal slits, it is difficult to realise how the necessary interchange through these slits can take place. Brown and Escombe* found that a leaf of *Catalpa bignioides* can absorb from ordinary air, containing 3 parts per 10,000 of carbon dioxide, about ·07 c.c. (N.T.P.) of carbon dioxide per square centimetre of leaf surface per hour. On each square centimetre there were 14,500 stomata, and each stoma, when fully open, had an area of ·0000618 square mm. Consequently the united area of the stomatal openings only amounted to ·9 % of the whole surface. Hence, if all the absorption took place by diffusion through these openings, diffusion of carbon dioxide through them must have taken place at the rate of about 7·77 c.c. per square centimetre per hour. With strong caustic soda solution they found that the rate of absorption of carbon dioxide from normal air by a free surface varied from ·12 c.c. to ·177 c.c. per square centimetre per hour. So that a leaf of catalpa in sunlight absorbs carbon dioxide at about half the speed at which it would if covered with a continually renewed film of caustic soda solution, and if all absorption occurs through the stomata the carbon dioxide must move about fifty times as fast through the openings as it would if they were filled with a strong solution of caustic soda.

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* Phil. Trans., vol. 186 (1895), 485.

Brown and Escombe have shown, however, that when an absorbent surface is covered with a diaphragm placed some distance above it the rate of diffusion of a gas from the outside air into the absorbing chamber *per unit area* increases enormously with a diminution of size of the aperture. This fact is understood by applying the kinetic theory of gases to the problem. The chance of any given molecule of carbon dioxide moving by virtue of its kinetic motion into the cell is proportional to the area of the opening; but once within the cell its chance of moving out again is less and less as the size of the aperture diminishes. Now the rate of diffusion through an aperture is the difference between the number of molecules which move in and out in a given time.

The number of molecules, so long as the temperature remains constant, moving inwards is solely dependent upon—

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* Phil. Trans., vol. 193 (1900), 223.

(1) The area of the aperture—say A.

(2) The partial pressure of the carbon dioxide in the atmosphere outside—say P.

The number of molecules moving outwards similarly depends upon—

(1) The area of the aperture—A.

(2) The partial pressure of the carbon dioxide in the chamber—say P′.

Let $x =$ number of molecules entering in one second and $y =$ number leaving in one second.

Then $x = k\text{AP}$
 and $y = k\text{AP}'$.

Of these quantities A is common, P is constant, about ·0003 of an atmosphere, but P′ depends upon the ratio of x to the rapidity with which the carbon dioxide is absorbed. This last will be proportional to the area of the absorbing surface—say S.

$$\therefore \quad \text{P}' = c\,\frac{k\text{AP}}{\text{S}}$$

Now the rate of diffusion is—

$$x - y = k\text{AP} - k\text{AP}'$$

$$= k\text{AP} - k\text{A}\left(c\frac{k\text{AP}}{\text{S}}\right).$$

Dividing by kP it is seen that the rate of diffusion is proportional to—

$$\text{A} - \frac{ck}{\text{S}}\,\text{A}^2$$

or, per unit area, to—

$$1 - \frac{ck}{\text{S}}\,\text{A}$$

Hence the smaller the value of the area of the aperture the greater is the amount of diffusion per unit area. The essential point in connection with this phenomenon is that by means of small apertures it is possible to have on the one side air containing practically its full amount of carbon dioxide, while on the other, the inside, the air is kept practically devoid of that gas; consequently very little diffuses outwards, provided the aperture be very small compared with the area of the absorbing surface.*

In the cases of the leaves of two plants, *Catalpa* and *Helianthus annuus*, Brown and Escombe made approximate measurements of the superficial area of the spongy absorptive surfaces of the cells of the parenchyma and of the area of the stomata opening into the space. They found a ratio in the case of the sunflower of about 212 : 1, in the case of catalpa of 1159 : 1.

In the case of helianthus the maximum rate of absorption of carbon dioxide by direct measurement was about ·134 c.c. per square centimetre of leaf surface per hour. This, according to Brown and Morris, would result if the partial pressure of the carbon dioxide within the intercellular space were reduced by only about 6%. If the absorption of carbon dioxide were perfect and able to keep the partial pressure at practically *nil* the amount of absorption of a helianthus leaf should be about 2 or 2·5 c.c. carbon dioxide per square centimetre per hour if the stomata be fully opened, or the area of the openings might be reduced to $\frac{1}{15}$ of their maximum and yet allow of the maximum observed absorption.

What has been said about absorbed carbon dioxide is equally true of the evolved oxygen in assimilation or of carbon dioxide in respiration.

Diffusion is also quite capable of accounting for the transpiration of water through the stomata, and the outward movement of water or oxygen would thus not interfere with the inward passage of the carbon dioxide.

With reference to the chemical reactions which attend the assimilation of carbon dioxide by plants much work has been done. The chlorophyll granules frequently enclose starch granules, and for a long time it was thought that starch was the first body formed in the assimilative act, and that sugar, also detected in leaves, was formed entirely from starch by hydrolysis.

It was shown in 1886 by Meyer† that leaves floated on solutions of sugar were able to produce starch. From levulose (10% solution) almost all the leaves tried produced starch, a smaller proportion were able to utilise dextrose, while still fewer could form starch from galactose. Baeyer in 1870 suggested that the formation of carbohydrates by leaves was probably effected by the formation of formaldehyde, $O{=}CH_2$, and its subsequent polymerization. Very little evidence in favour of this view was forthcoming, however; indeed Bokorny in 1888* showed that formaldehyde itself would not act as a source of starch owing to its poisonous action. In 1891† he succeeded in using as a nutrient a dilute solution of sodium oxymethylsulphonate, $CH_2(OH).SO_3Na$, which readily splits up into formaldehyde and sodium hydrogen sulphite—

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* This explanation, based on the kinetic theory of gases, appears to the author to be clearer and more in accordance with what he believes to be the true mechanism of the phenomenon than the more elaborate and more mathematical conception described by Brown and Escombe, in which the process of diffusion is pictured as analogous to a flux or flow of carbon dioxide through the aperture.

† Bot. Zeit. 1886, Nos. 5 & 6; J.C.S. 1886, abst. 902.

$$CH_2(OH).SO_3Na = OCH_2 + NaHSO_3.$$

By the addition of sodium or potassium phosphate the injurious effect of the acid sulphite upon the plant could be prevented, and he then found that the leaves of *Spirogyra majuscula* were able to form starch from a very dilute solution of this formaldehyde derivative. Baeyer's hypothesis was thus confirmed.

According to Brown and Morris‡ cane sugar is probably the first sugar formed in the process of assimilation. Its formation proceeds until the cell-sap attains a certain concentration, varying in different plants, when starch granules begin to form from it. These are intended as reserve materials and become attacked by the diastase, present in all leaves, as soon as the sugar solution, by diffusion to other portions of the plant, sinks below a certain concentration. They think that inversion of the cane sugar into dextrose and levulose precedes its translocation from cell to cell and that maltose is the chief product of the diastatic action on starch; that of the invert sugar formed in the plant the dextrose is first used up in respiration and tissue formation, and consequently that levulose enters the stem of the plant in larger quantities than dextrose.

The formation of carbohydrates, though perhaps the most important function of the leaves, is by no means their only one.

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* Landwirt. Versuchs-Stat. 1889.

† Ber. deut. bot. Gesell. 1891, 103.; J.C.S 1891, abst. 1539.

‡ Jour. Chem. Soc. 1893, Trans. 604.

In addition there are two processes which may be briefly described—transpiration of water and formation of nitrogenous organic substances.

Transpiration is effected, as already stated, chiefly through the stomata; but exhalation of aqueous vapour occurs from almost all parts of the exposed parts of plants. The activity of transpiration depends chiefly upon the temperature, the humidity of the air, and the amount of light received by the plant. It is increased by a rise of temperature or by brighter light, but diminishes with greater humidity of the air around. It is also regulated by the size of the apertures—the stomata—through which the greater quantity of the transpiration is effected. These openings are altered in size according to the greater or less turgidity of the guard cells.

In consequence of this escape of water from the leaves, a diminished pressure is often set up in the upper parts of a plant, so that the root pressure is aided in driving water from below. Transpiration is thus active in producing the rise of sap and the consequent bringing up of the mineral matters absorbed by the roots into the leaves, there to be elaborated into nutritive materials.

The amount of water evaporated by a plant increases if the soil water or culture fluid is very dilute. Oats were found to evaporate 515 grammes of water for each gramme of dry produce when grown in a 3% nutritive solution, but 688 grammes of water in 0·25% solution.*

The building up of nitrogenous, proteid matter from carbohydrates and nitrates or ammonium salts is not thoroughly understood. It is generally stated that the presence of light is essential to this process and that the production of proteids from nitrates and sulphates requires the energy of light to bring about the necessary reduction of nitrogen and sulphur from their oxidised compounds.† Experiments made recently, especially in Japan, show that barley, French beans, and potatoes are able to produce proteids from nitrates in complete darkness, provided they be supplied with a sufficient amount of sugar; with small quantities of sugar no proteids were formed. Hence the necessity of light in proteid formation really depends upon the production of abundance of carbohydrates. Asparagine is probably an intermediate product between nitrates and proteids and accumulates in the plant if the conditions for proteid production are not favourable.*

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* **Heinrich, Ann. Agron. 1897, 186; J.C.S. 1897, abst. ii. 424.**

† **v. Godlewski, Jour. Chem. Soc. 1897, abst. ii. 583.**

Since asparagine seems undoubtedly to be produced from proteids when translocation of nitrogenous matter takes place, it appears that amides are products both of anabolism and katabolism. It has been shown that in many plants the leaves cut in the morning contain much less starch and nitrogenous material than similar leaves cut in the evening, proving that during the night there is a transference of starch and albuminoids, stored during the day in the leaves, to other parts of the plant.†

The Flowers and Seeds.—The formation of flowers and seeds is a process which in many plants is the final act of their vitality. During flowering, true respiration, *i.e.*, oxidation of carbonaceous matter and evolution of carbon dioxide, takes place more rapidly than usual, and in some cases to an extent sufficient to bring about a sensible rise of temperature. It must be remembered that respiration goes on during the whole of a plant's active existence, but during daylight is more than counterbalanced by the assimilative process already described.

In certain plants—*biennials*—preparation for the great work of seed formation occupies the whole of their first year's life. A large store of reserve material is accumulated, either in the root or stem, and during the second year this is utilised in the production of a flower stem and seeds.

During the formation of seed a concentration of nutritive matter from the stem, root, and foliage into the seed takes place, and the main portions of the plant are thus robbed of most of their important constituents. In many plants the maximum amounts of nutritive matters are found in the leaves, stems, &c., immediately before flowering.

A store of food material, intended for the nourishment of a new plant, accumulates in the seed. Albuminoids are always present, together with phosphorus, sulphur, potassium, chlorine, and the other elements essential to plant life. Of carbonaceous matter, however, two varieties occur. Some seeds contain large amounts of carbohydrates, chiefly starch, while others are practically devoid of starch, but contain fats or oils in large proportion.

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* Kinoshita, J.C.S. 1896, ii. 54; Suzuki, J.C.S. 1899, 323.

† Suzuki, J.C.S. 1897, abst. ii. 580.

CHAPTER XI.

CROPS.

In this chapter a brief account is given of the proximate composition of some of the chief crops grown on a farm managed according to the usual English methods.

Crops may conveniently be divided into the following classes :—

(1) Grain crops, in which the seed is the portion of the plant most valued.
(2) Root crops, in which the root or tuber is the valuable product.
(3) Fodder crops, in which the stem and foliage are of most importance.

(1) GRAIN CROPS.—The most important of these are—

(a) Cereals—maize, wheat, rye, barley, and oats.
(b) Leguminous plants—beans, peas.

(a) The Cereals.—These are characterised by containing much less nitrogen than leguminous or root crops, and by the richness of their seed in carbohydrates, particularly starch.

They are also remarkable for the large amount of silica which is usually present in the outer portions of the leaves and straw. This silica, which is apparently not essential, is absorbed as soluble silicates, the metals, probably chiefly potassium, being used in the plant, the silica being thus merely an excretion. Potash and lime are also present to a less extent in cereals than in other farm crops. Owing to their modest demands for potash, lime, and nitrogen, cereals will grow for many seasons in succession upon soil which has become so exhausted as to yield little or no return when planted with leguminous or root crops. They, however, appear to depend for their nitrogen entirely upon nitrates in the soil, and as their growth is practically over before the great season for nitrification begins, they derive great benefit from nitrogenous manures.

Wheat, being usually autumn sown, has a longer period of growth than barley or oats and is consequently better able to supply itself with the necessary food from the soil. With a wheat crop, however, the land loses the spring tillage, which is conducive to nitrification, and therefore nitrogenous manures are perhaps more required by wheat than by the other cereals.

Wheat straw is remarkable for the excessively large amount of silica and small amount of nutritive matter which it often contains.

Wheat is particularly fitted for human food owing to the light, spongy, and palatable bread which can be made from wheat flour. This is due to the richness of the grain in *gluten* and the peculiarity of this gluten as compared with that occurring in the other cereals.*

Rye very much resembles wheat in its chemical composition and manurial requirements.

Barley and *oats* have a much shorter period of growth and hence require an abundance of plant food. Like the other cereals, they can only obtain nitrogen from nitrates; but the spring tillage in preparing the land for sowing renders it also very suitable for the development of the nitrifying organisms. Moreover, in the case of barley for malting the presence of too much nitrogenous food in the soil favours the production of albuminoids in the grain so as to render it unsuitable for brewing purposes. Consequently nitrogenous manures, in the case of barley, require to be applied in moderation only. The grain of oats is especially rich in ash; their straws are more nutritious, digestible, and palatable to animals than those of wheat and rye.

Maize, which is not often grown in England, and then generally for fodder, has the advantage over other cereals of prolonging its growth until late in the autumn, so that it has the opportunity of assimilating the nitrates produced during the hot season. The grain is particularly rich in starch and fat.

(b) Leguminous Grain Crops.—*Beans* and *peas*. The characteristic of these plants is their power of obtaining the large amounts of nitrogen which they contain, from the air, under certain favourable conditions which have been already described.* They contain more than twice as large a proportion of nitrogen as the cereals and also much larger amounts of potash and lime, but very little silica. The seeds are remarkable for the large amounts of an albuminoid—legumin—analogous to casein, which they contain; there is also present considerable quantities of the fat-like body, lecithin.†

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* *v.* Chap. IX., p. 215.

(2) ROOT CROPS.—*Turnips, swedes, mangolds, potatoes.* These crops are characterised by the large amounts of nitrogen (much of which, however, is present as amides and often as nitrates) and mineral matter which they contain. They are also remarkable for the high percentage—sometimes 90 % or over—of water which is contained in their "roots" or tubers.

Turnips and swedes depend chiefly upon the surface soil and have but limited powers of attacking the insoluble phosphates, though able generally to provide themselves with potash. Phosphatic and nitrogenous manures are therefore usually most effective.

Mangolds are deeper rooted and generally able to provide themselves with food, nitrogen being the constituent most likely to be lacking. Being rich in ash constituents and heavy croppers, mangolds are probably the most exhausting crop grown. A peculiarity of mangolds is the benefit they receive from applications of common salt.

Beets, which resemble the mangold in many respects, are, on the Continent, largely grown for sugar. Small beets yield a higher percentage of sugar than large ones.

Indeed, in the case of all roots the large, well-developed ones produced by liberal manuring are found generally to be more watery, to contain less sugar and starch, and altogether to be less nutritious than small ones. Turnips, swedes, and mangolds contain sugar in large quantities (5 to 8 %).

Potatoes are chiefly limited to the surface soil for their food. They are rich in starch, for which reason, perhaps, they require considerable quantities of potash to assist in its assimilation. They are also benefited by liberal general manuring, and farm-yard manure yields excellent results with this crop, especially in somewhat dry seasons, when the water-retaining power of the organic matter of the manure is of great value. In connection with the use of potash manures it is found that the sulphate is preferable to the chloride, the latter tending to injure the quality of the potatoes, rendering them waxy. A similar preference for the sulphate exists in the case of beet.

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* *v.* Chap. IV., p. 80.

† *v.* Chap. IX., p. 206.

(3) FODDER CROPS.—In these the seeds are of little importance, the foliage and stems being the main parts. They include gramineous (grasses), leguminous, and other plants.

Meadow Hay.—This crop consists of a very variable mixture of different plants. The grasses are usually predominant in quantity, and they, in general chemical properties, resemble the cereals. Their ash is rich in silica and potash, but poor in lime; while in the organic portion they contain comparatively little nitrogen, but are rich in carbohydrates. The roots of grasses are mainly confined to the surface soil, so that application of manure must be made if grass land is not to diminish in fertility. Moreover, the root débris of grass land by its accumulation, gradually produces a peaty or humic character in the upper portion of the soil, with consequent nitrification and loss of calcium. Hence manuring with bones, lime, or basic slag, or other calcareous substances is generally advantageous.

Liberal additions of nitrate of soda, potash salts, and phosphates produce very heavy crops of hay by encouraging the growth of coarse grasses; but clover and some of the finer grasses are thereby diminished and the quality of the hay deteriorates.

Leguminous Crops, *e.g.*, clovers, trefoil, lucerne, &c., are also present in ordinary grass land, but in varying amount. These fodder leguminous crops have the same general characteristics as the leguminous grain crops. Their growth is greatly favoured by additions of potash and lime compounds and by stinting the nitrogenous manuring; the clovers, &c., having an independent supply of nitrogen, are thus able to outgrow their competitors, the grasses. As already stated, leguminous plants are remarkable for the large amounts of nitrogenous matter, lime, and potash which they contain. The lime is mainly contained in the leaves. Silica is almost absent. Clover, lucerne, &c., are also grown as crops upon arable land with valuable after-effects. The land is thereby actually enriched in nitrogen, notwithstanding the fact that a very large amount of nitrogen is removed in the crop. The nitrogen is obtained from the air in the manner already described. The beneficial effect of the growth of clover upon the soil has long been known and utilised in agriculture; but it was not until after many laborious researches had been made that the explanation of the fact was discovered by Hellriegel and Willfarth about 1888.*

By repeated cropping of land with clover a condition known as "clover sickness" is often set up. The seed in the summer germinates and grows well until the autumn or winter, when the plants die off rapidly, and, in many cases, a minute eelworm attacks the root and stem. Whether these nematoids *(Tylenchus)* are the cause or a consequence of the disease appears to be uncertain. Clover sickness has also been ascribed to certain fungi. It is said that deficiency of the soil in potash and lime is a predisposing cause of this disease.

Other plants are sometimes grown for fodder, *e.g.*, rye, vetches, oats, &c.

In some cases the fodder crop is eaten green by animals; but in most cases it is preserved for future use, either by being made into *hay* or *silage*.

Hay-making consists in drying the plants by exposure to sun and air to such an extent as to greatly check fermentation, which, in the presence of moisture, soon occurs in vegetable matter. This fermentation is due to the action of micro-organisms and is accompanied by absorption of oxygen from the air and consequent evolution of heat. During hay-making the most important change is the loss of water; this naturally varies considerably with the nature of the crop, its ripeness, &c. Ordinary meadow grass will usually contain about 75% of water, while the hay from it, in the stack, may contain about 16%. One hundred tons of grass will yield from 30 to 40 tons of hay, while the same weight of freshly cut clover will yield on an average about 33 tons of hay.

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* *v.* p. 80.

Of great importance is the time of cutting. Since fodder crops are essentially straw, the proper time is before the nutrient ingredients are moved from the foliage into the seed. Hence hay should be cut when the grasses are flowering. If grass is left until too ripe, the resulting hay is found to be poorer in albuminoids and ash, though richer in carbohydrates and indigestible fibre.

The changes in *Timothy grass* during ripening are well seen from the following table*:—

Date of cutting.	Hay, per acre. lb.	Protein. lb.	Fibre. lb.	N-free extract. lb.	Ether extract. lb.	Ash. lb.
June 26 ...	4480	240	1056	1602	165	224
July 2 ...	4320	225	1155	1663	152	228
July 11 ...	5240	246	1380	1960	153	273
July 23 ...	5180	253	1377	2058	137	239

It will be seen that the nitrogenous matters are practically not increased by the latter growth, but that carbohydrates and fibre are largely added to after blossoming. On June 26th the grass was in full bloom; on July 23rd its seeds were almost ripe.

Grass and clover are always abundantly supplied with micro-organisms, including bacteria, moulds, yeasts, &c.; these act upon the sap and woody fibre of the grass when cut, producing oxidation and evolving carbon dioxide and small quantities of other gases. The act of oxidation is attended with the evolution of heat. These changes take place in the open air with little rise of temperature, because the heat is carried away by conduction and convection almost as fast as it is evolved. Moreover the activity of the micro-organisms soon diminishes if the materials dry.

An investigation into the changes produced in grass by fermentation was made in 1897 by Emmerling.† Freshly cut grass of the following composition calculated on the dry matter—

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* Hunt, Bulletin 5, U.S. Dept. of Agriculture.

† Ber. 1897, 1869; J.C.S. 1897, abst. ii. 579.

	%
Proteids	11·80
Ash	7·62
Ether extract ...	1·86
Woody tissue ...	26·40
Non-nitrogenous extract	52·32
	100·00

—was placed in a large vessel provided with thermometer and delivery tube. In 24 hours the temperature rose several degrees; during four weeks a slow current of carbon dioxide (64 %) and nitrogen (36 %) was evolved.

The grass at this point had the composition:—

	%
Proteids	9·13
Ash	8·14
Ether extract ...	3·24
Woody tissue ...	31·36
Non-nitrogeous extract...	48·13
	100·00

It had a pleasant hay-like odour. Many moulds, bacteria, and micrococci were observed. The increase in the ether extract is attributed to organic acids formed from the carbohydrates.

No doubt such changes as above described take place during the process of hay-making; but usually they can only proceed to a very limited extent, owing to the desiccation of the grass by sun and wind.

When the partially dried grass is collected in stacks or barns, however, further desiccation is almost prevented, and the processes of fermentation recommence. If the hay still contain much moisture these processes proceed so rapidly that the very limited circulation of air in the stack does not carry the heat away as fast as it is produced, the temperature rises, fermentation is thereby favoured, and the temperature gets higher and higher.

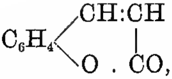
While most organisms are killed by a temperature about 60°, it has been shown that certain bacteria present in surface soil can work energetically at 70° or higher. Eventually, however, even they will be killed by the high temperature, and direct oxidation of some substances of the hay must then commence.

A further exaltation of temperature then ensues until, under favourable conditions, the actual ignition point of the hay is reached and the mass begins to inflame. Generally, however, the highest temperature is reached near the centre of the stack, where access of air is difficult and slow; consequently a smouldering combustion rather than actual flaming results.

The conditions most favourable to the dangerous heating of haystacks are not exactly known, but undoubtedly the presence of a certain amount of moisture is one of the most important. Obviously, then, one of the best methods of preventing the firing of haystacks is to thoroughly dry the hay before stacking it. This cannot always be done, nor is it entirely satisfactory, for if over-dried it does not ferment sufficiently to develop the aroma, flavour, and colour which are desirable in good hay. If hay has to be stacked while somewhat green, one of two methods is generally adopted:—

(1) To mix salt with it. This probably acts by preventing or hindering the growth of the micro-organisms. At the same time it renders the hay more palatable and also probably lessens the risk of its becoming mouldy.

(2) To ventilate the stack. This is probably the more efficient method. It is generally effected by including in the hay at the time of stacking a sack or sacks filled with hay, placed vertically and drawn upwards from time to time as the stack rises. Another method, often employed in Scotland, is to erect, in the centre of the site chosen for the stack, an open conical structure composed of wooden scantlings meeting at a point. The stack is then built round and above this. These methods depend for their efficiency not upon checking the heat production, as the first one does, but upon the removal of the evolved heat by circulation of air.

The odour of hay, upon which its palatability largely depends, is probably due partly to the products of fermentation, among which compound ethers are probably present, and partly to *coumarin*, $C_9H_6O_2$, or  $C_6H_4\left\langle\begin{array}{l}CH{:}CH\\ \qquad|\\ O\ .\ CO,\end{array}\right.$ which occurs in woodruff *(Asperula odorata)*, in Bokhara clover *(Melilotus)*, in sweet-scented vernal grass *(Anthoxanthum odoratum)*, and probably in many other plants.

Coumarin is a crystalline solid with a characteristic odour (that of new-mown hay), is slightly soluble in water, and very soluble in alcohol. Its odour becomes very pronounced when plants containing it are dried.

Ensilage or **Silage** is made by preserving green fodder in a closely compacted condition so as to prevent access of air as much as possible and so hinder the various fermentative changes from proceeding beyond a certain stage. Originally all silos consisted of pits or buildings of stone or wood, in which the materials could be stored and subjected to high pressure. It is now a common practice to simply stack the fodder in the green state, treading or pressing it down as much as possible, and finally weighting it with stones or earth. In all cases the outside of the silo, where air has access, becomes so rotten as to be useless, but the amount of waste is not very great.

The changes which occur in the silo are in many respects similar to those in the stack, but fermentation is limited in a different manner—by air exclusion, while in a stack it is chiefly from lack of sufficient moisture. Consequently it is found that the relative progress of different organisms is different in the two cases. Moreover, in a silo the predominant character of the fermentation, and consequently of the silage, depends largely upon the management. If the silo be made slowly, so that a considerable amount of heating may occur before the weighting expels the air, the temperature rises so high (up to 55° or 60°) that the bacteria which produce acids (*e.g.*, acetic, lactic, and butyric acids) are destroyed. The resulting product is then known as "sweet" silage. If the silo be built with little delay and compressed at once the temperature does not rise so high, and the acetic, lactic, and other acid-producing bacteria are not killed, but produce their characteristic products, thus leading to the formation of "sour" silage.

The changes in composition which fodder undergoes during fermentation in a silo lead to a loss of carbohydrates, partly as gaseous products and partly by conversion into insoluble "fibre." Except by mechanical loss, say by juices running from the silo, the mineral matter undergoes no change; the albuminoids are slightly lessened, probably by conversion into amides, and even into ammonium salts.

The composition of clover and rye grass, when cut and after being in the silo for 90 days, is given by Wilson and Harper* as follows:—

	Clover (mean of 8 analyses).		Rye grass.	
	Fresh.	Silage.	Fresh.	Silage.
Water	79·5	80·1	47·1	74·3
Solids	20·5	19·9	52·9	25·7
The solids dried at 100°				
Albuminoids	16·5	17·4	8·5	7·1
Non-albuminoid N × 6·25 ...	3·9	4·5	3·6	2·9
Carbohydrates (by difference)	46·3	37·5	48·8	45·7
Fibre	23·8	30·2	30·5	36·8
Ash	9·5	10·5	8·6	7·5
% non-albd. N of total N.	19·0	20·6	30·1	28·9

They calculate the following:—

	Albuminoids.	Non-alb. N × 6·25	Carbohydrates.	Fibre.	Ash.	Total.
100℔. dry matter of clover when put into silo contain	16·5	3·9	46·3	23·8	9·5	100·0
Ditto, when taken out	15·7	4·0	33·9	27·4	9·5	90·5

Experiments were also made on the digestibility of the albuminoids of the fresh fodder and the silage, using "pepsin" and "pancreatine." The following table gives their results:—

	Fresh fodder. In 100 parts of dry matter.			Silage. In 100 parts of dry matter.		
	Total albuminoids.	Albds. indigestible in pepsin & pancreatine.	Percentage of true albds. digested.	Total albuminoids.	Albds. indigestible in pepsin & pancreatine.	Percentage of true albds. digested.
Clover (mean of 8)	16·6	3·06	81·5	17·4	7·5	56·4
Rye grass ...	8·5	1·84	78·3	7·1	3·2	54·2

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* Jour. Soc. Chem. Ind. 1891, 115.

Thus though the loss in albuminoids is very small the diminution in digestibility is serious. The authors suggest that silage should only be made of fodder comparatively low in albuminoids and that clover and other highly nitrogenous crops should be either used as pasture or made into hay.

The table on pages 251, 252, and 253, containing the results of American investigations, may be useful.* The figures in the last three columns, giving the percentage amounts of valuable manurial constituents, have evidently not been derived from the analyses of the same samples which yielded the other numbers, as there are numerous cases in which the results are inconsistent.

A few remarks about the usual method of analysing crops and other food stuffs may here be given. Almost all analyses of food which have been published until quite recently were made by a method introduced by Henneberg in 1864, generally known as the "Weende" method. According to this method the constituents are reported as—

Water.
Proteids or nitrogenous matters.
Fat or ether extract.
"Nitrogen-free extract" or "soluble carbohydrates."
Crude fibre.
Ash.

The water and ash are determined by general methods, the nitrogenous matter by a determination of the total nitrogen and multiplying this by 6·25, and the "fat" by ether extraction. The "crude fibre" is then determined by treating a portion of the sample from which the fat has been extracted with boiling dilute sulphuric acid (containing 1·25 % real acid) for half an hour, washing the residue until free from acid, and again boiling for half an hour with a solution containing 1·25 % of sodium hydrate. The whole is then filtered and the residue thoroughly washed, dried at 110°, and weighed. The residue is next completely incinerated, when the loss of weight gives the "fibre."

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* Bulletins Nos. 11 and 15, Office of Experiment Stations, U.S. Dept. of Agriculture.

COMPOSITION OF CROPS.

Grain Crops.

	Water.	Ash.	Protein.	Fibre.	N-free extract.	Fat.	Potash.	Phosphoric acid.	Nitrogen.
Wheat	10·5	1·8	11·9	1·8	71·9	2·1	0·5	0·79	2·36
Rye	11·6	1·9	10·6	1·7	72·5	1·7	0·54	0·82	1·76
Barley	10·9	2·4	12·4*	2·7	69·8	1·8	0·48	0·79	1·51*
Oats	11·0	3·0	11·8	9·5	59·7	5·0	0·62	0·82	2·06
Maize	10·9	1·5	10·5	2·1	69·6	5·4	0·40	0·70	1·82
Rice	12·4	0·4	7·4	0·2	79·2	0·4	0·09	0·18	1·08
Buckwheat ...	12·6	2·0	10·0	8·7	64·5	2·2	0·21	0·44	1·44
Horse beans ...	11·3	3·8	26·6	7·2	50·1	1·0	1·29	1·20	4·07
Peas	10·5	2·6	20·2	14·4	51·1	1·2	0·99	0·82	3·08
Linseed ...	9·2	4·3	22·6	7·1	23·2	33·7	1·03	1·39	3·61
Cotton seed ...	10·3	3·5	18·4	23·2	24·7	19·9	1·17	1·27	3·13
Sunflower seed ...	8·6	2·6	16·3	29·9	21·4	21·2	0·56	1·22	2·28

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* These numbers are not in agreement with each other or with English analyses. The average would probably be 10·5 for protein and 1·70 for nitrogen.

	Water.	Ash.	Protein.	Fibre.	N-free extract.	Fat.	Potash.	Phosphoric acid.	Nitrogen.
Root Crops.									
Potatoes ...	78·9	1·0	2·1	0·6	17·3	0·1	0·46	0·12	0·32
Beets	88·5	1·0	1·5	0·9	8·0	0·1	0·44	0·09	0·24
Mangolds ...	90·9	1·1	1·4	0·9	5·5	0·2	0·38	0·09	0·19
Turnips ...	90·5	0·8	1·1	1·2	6·2	0·2	0·39	0·10	0·18
Swedes	88·6	1·2	1·2	1·3	7·5	0·2	0·49	0·12	0·19
Carrots	88·6	1·0	1·1	1·3	7·6	0·4	0·51	0·09	0·15
Parsnips ...	88·3	0·7	1·6	1·0	10·2	0·2	0·44	0·20	0·18
Artichokes ...	79·5	1·0	2·6	0·8	15·9	0·2	0·47	0·14	0·26
Fodder Crops.									
Pasture grass ...	80·0	2·0	3·5	4·0	9·7	0·8	0·75	0·23	0·91
Timothy ,, ...	61·6	2·1	3·1	11·8	20·2	1·2	0·76	0·26	0·48
Green oats ...	62·2	2·5	3·4	11·2	19·3	1·4	0·38	0·13	0·49
Green rye ...	76·6	1·8	2·6	11·6	6·8	0·6	0·73	0·15	0·33
Meadow fescue ...	69·9	1·8	2·4	10·8	14·3	0·8			
Italian rye grass ...	73·2	2·5	3·1	6·8	13·3	1·3	1·14	0·29	0·54
Red clover ...	70·8	2·1	4·4	8·1	13·5	1·1	0·46	0·13	0·53
Crimson clover ...	80·9	1·7	3·1	5·2	8·4	0·7	0·49	0·13	0·43
Lucerne ...	71·8	2·7	4·8	7·4	12·3	1·0	0·56	0·13	0·72
Alsike clover ...	74·8	2·0	3·9	7·4	11·0	0·9			

	Water.	Ash.	Protein.	Fibre.	N-free extract.	Fat.	Potash.	Phosphoric acid.	Nitrogen.
Silage.									
Red clover ...	72·0	2·6	4·2	8·4	11·6	1·2			
Rye	80·8	1·6	2·4	5·8	9·2	0·3			
Maize	79·1	1·4	1·7	6·0	11·0	0·8	0·37	0·11	0·28
Hay.									
Mixed grasses ...	15·3	5·5	7·4	27·2	42·1	2·5	1·55	0·27	1·41
Timothy ...	13·2	4·4	5·9	29·0	45·0	2·5	0·90	0·53	1·26
Meadow fescue ...	20·0	6·8	7·0	25·9	38·4	2·7	2·10	0·40	0·99
Italian rye grass ...	8·5	6·9	7·5	30·5	45·0	1·7			
Red clover ...	15·3	6·2	12·3	24·8	38·1	3·3	2·20	0·38	2·07
White clover ...	9·7	8·3	15·7	24·1	39·3	2·9	1·81	0·52	2·75
Crimson clover ...	9·6	8·6	15·2	27·2	36·6	2·8	1·31	0·40	2·05
Lucerne ...	8·4	7·4	14·3	25·0	42·7	2·2	1·68	0·51	2·19
Vetch	11·3	7·9	17·0	25·4	36·1	2·3			
Straw.									
Wheat	9·6	4·2	3·4	38·1	43·4	1·3	0·51	0·12	0·59
Rye	7·1	3·2	3·0	38·9	46·6	1·2	0·79	0·28	0·46
Barley	14·2	5·7	3·5	36·0	39·0	1·5	2·09	0·30	1·31
Oats	9·2	5·1	4·0	37·0	42·0	2·3	1·24	0·20	0·62
Horse beans ...	9·2	8·7	8·8	37·6	34·3	1·4			

The method used in the determination of the remaining item, "the nitrogen-free extract," in these analyses is least satisfactory of all—being simply to take the difference between the sum of the percentages of the other constituents and 100.

In the form just described thousands of analyses have been published, and though the results are of considerable value they cannot be considered satisfactory.

Water.—The assumption that only water is expelled by heating a food to a temperature of about 100° is certainly not warranted, as many organic compounds undergo change below this temperature; moreover, many fats and oils absorb oxygen and consequently increase in weight when exposed to air. The latter objection can be overcome by drying in a current of hydrogen.

Ash.—In this case, as in all vegetable and animal matter, the ash left on incineration has not the composition of the inorganic compounds present in the plant or animal. This objection, however, is not a very important one.

Fat.—Since this is really the matter soluble in ether, it is better described as "*ether extract.*" In the case of many substances, chorophyll, resins, waxes, and organic acids, *e.g.*, lactic acid, are dissolved by ether and are included in the "ether extract." In some instances the amounts of these non-fatty substances may be considerable in proportion to the true fat.

Nitrogenous matter.—However accurate the determination of nitrogen may be, the figures given under this head can never be very trustworthy. In the first place *all* the nitrogen in a substance is not usually present as albuminoids, but may be partly as amides, ammonium salts, or nitrates. Then, too, all albuminoids do not contain the same proportion of nitrogen* and therefore multiplying by 6·25 does not give a correct measure of their amount. A method of distinguishing between the nitrogen existing as true albuminoids and that as amides, &c., has already been described.†

Crude fibre.—The method used in the estimation of this material is obviously based upon an assumption that from a material freed from fat by ether extraction dilute sulphuric acid and dilute sodium hydrate will effect the solution of all matter which could be removed in the digestive processes of an animal; it evidently cannot yield any really satisfactory results. Moreover, the amount of the "fibre" obtained depends very much upon the state of subdivision of the material and other circumstances, and the residue obtained often contains nitrogenous substances.

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* See p. 216.

† See p. 219.

Non-nitrogenous extractives.—This item, like all those obtained by difference, is liable to the accumulated errors of all the direct determinations, some of which, *e.g.*, the fibre, are probably very great.

According to Stone* the results obtained by the Weende method are very incorrect. He examined specimens of wheat and maize, both by the usual conventional methods and by determining the various carbohydrates actually present. Some of the results by the two methods are given below.

Air-dry material (per cent.) :—

	Water.	Ash.	Fat.	Fibre.	Protein.	N-free extract.
Winter wheat ...	6·28	2·14	1·83	2·85	14·68	72·22
Spring wheat ...	8·55	1·43	2·00	2·77	14·22	71·03
Maize meal ...	12·43	1·51	3·80	2·35	11·60	68·31

Under the last column (obtained by difference) it is generally assumed that starch, digestible cellulose, and sugars are included.

By actually determining the percentages of the various carbohydrates, Stone obtained the following numbers :—

	Winter wheat.	Spring wheat.	Maize meal.
Cane sugar ...	0·48	0·66	0·24
Invert sugar ...	0·08	None	None
Dextrin ...	0·25	0·38	0·28
Starch ...	28·73	27·36	37·28
Pentosans ...	4·54	3·94	4·09
Cellulose ...	2·68	2·26	1·93
	36·76	34·60	43·82

It is thus evident that 35 or 36% in the case of wheat and about 24·5% in the case of maize of the whole material is not estimated and exists in the plant in some other form than those of the carbohydrates mentioned.

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* Bulletin No. 34 (1896), Office of Experiment Stations, U.S. Dept. of Agriculture.

This is a remarkable result, and the subject merits further investigation.

In many instances in modern analyses the amounts of pentoses and pentosans in foods are determined. The latter appear to be much less digestible than the other carbohydrates.*

The following analyses† will illustrate the occurrence of pentosans in fodders :—

	Protein, N × 6·25.	Ether extract.	Ash.	Crude fibre free from pentosans.	N-free extract free from pentosans.	Pentosans, furfuraldebyde × 1·84.	Dry matter.
Meadow hay	11·70	3·60	7·03	21·09	37·63	18·95	93·26
Clover hay	13·90	2·31	6·01	33·74	28·00	16·04	92·04
Rye straw	3·24	2·28	4·31	37·61	23·47	29·09	93·20
Lupin straw	5·80	1·36	3·76	45·34	22·91	20·22	92·80

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* Stone, Agri. Sci. 7, 6.

† Düring, Jour. Chem. Soc. 1897, abst. ii. 588.

CHAPTER XII.

THE ANIMAL.

THE body of an animal, from a chemical standpoint, consists of a very intimate mixture of compounds, some of which are little understood and apparently highly complex in character. The body may be considered as made up of lifeless products of metabolism (*e.g.*, fat cells, horny matter, earthy portions of bone, &c.) permeated by the really living substance, protoplasm. The latter is highly aqueous and contains proteids, with smaller quantities of carbohydrates, fats, and salts.

The elements contained in the animal body are the same as those found in plants, but their relative proportions differ considerably. Sodium, chlorine, and fluorine particularly appear to be of much more importance to animals than to plants.

The proximate constituents of animals also resemble those of plants.

They may be divided into—

(1) *Inorganic compounds*, consisting mainly of water, various acids (*e.g.*, hydrochloric acid), ammonia, and numerous salts (*e.g.*, calcium phosphate, sodium chloride, &c.).

(2) *Organic compounds*—
   (a) Proteids, *e.g.*, albumin, myosin.
   (b) Amides, *e.g.*, urea.
   (c) Fats.
   (d) Carbohydrates, *e.g.*, glycogen.
   (e) Other compounds.

The general characteristics of some of these substances have been given in the chapter on the constituents of plants. Reference must be made to some work on physiological chemistry for further details.

The chemical composition of the whole bodies of animals was investigated by Lawes and Gilbert in 1848-1859.*

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* Jour. Roy. Agric. Soc. 1895.

The following table embodies some of their results :—

Percentage composition of the whole bodies of animals.

Description of animal.	Water.	Fat.	Nitrogenous matter.	Ash.	Contents of stomach and intestines in moist state.
Fat calf ...	63·0	14·8	15·2	3·80	3·17
Half-fat ox ...	51·5	19·1	16·6	4·66	8·19
Fat ox ...	45·5	30·1	14·5	3·92	5·98
Fat lamb ...	47·8	28·5	12·3	2·94	8·54
Store sheep ...	57·3	18·7	14·8	3·16	6·00
Half-fat sheep ...	50·2	23·5	14·0	3·17	9·05
Fat sheep ...	43·4	35·6	12·2	2·81	6·02
Store pig ...	55·1	23·3	13·7	2·67	5·22
Fat pig ...	41·3	42·2	10·9	1·65	3·97

It will be seen from the above figures that the nitrogenous matter is the most constant in quantity and that the water and fat vary inversely with each other. The amount of ash is chiefly dependent upon the proportion of bones to the rest of the body.

Among the most important parts of the animal body the following may be mentioned :—

(1) The blood.
(2) The bones.
(3) The muscles.
(4) The connective tissues.

Blood consists of a transparent colourless liquid, the *blood plasma*, in which an immense number of solid particles, the *red and colourless corpuscles*, are suspended. When taken from the body, unless special precautions are observed, blood coagulates or clots with a rapidity which varies with different animals and also with the temperature; if cooled quickly coagulation is retarded; the blood of the horse coagulates more slowly than that of other animals.

In clotting, a separation into a clear yellow liquid—*blood serum*—and a red solid—*blood clot*—occurs. This separation is brought about by the coagulation of a proteid—*fibrinogen*—

which exists in blood plasma and which can be removed by beating the blood during clotting. Blood serum thus differs from blood plasma in containing no fibrinogen and a smaller quantity of calcium, magnesium, and phosphoric acid.

Blood serum is of a sticky consistency, of alkaline reaction, and has a specific gravity of about 1·028. It contains fats, soaps, cholesterol, $C_{26}H_{43}OH$, lecithin, $C_2H_4(OH)(CH_3)_3N.HPO_4.C_3H_5{:}(C_{18}H_{35}O_2)_2$, albuminoids, glucose, traces of urea, uric acid, creatin, lactic acid, and hippuric acid.

The following analyses of serum were made by Hammarsten :—

Serum from blood of—		Total solids.	Total albuminoid substances.	Fat, lecithin, salts, &c.
Man	...	9·20	7·62	1·59
Horse	...	8·60	7·26	1·34
Ox	...	8·97	7·50	1·47
Hen	...	5·40	3·95	1·45

The ash of serum (about ·85 %) consists chiefly of common salt (·6 to ·7 %), with small quantities of potash, lime, and magnesia.

The rapidity with which blood coagulates after leaving the body varies, as already stated, with different animals and with the conditions under which it is kept. Coagulation is retarded by cooling, by diminishing the amount of oxygen or increasing that of carbon dioxide, by the addition of acids, alkalies, egg-albumen, sugar, gum, glycerine, or oil. Coagulation is facilitated by warmth, by contact with foreign bodies (*e.g.*, by stirring or beating), by free admission of air, by addition of a small quantity of water, or by the addition of ferric salts, alum, &c.

The spontaneous clotting of blood after removal from the animal is assigned to different causes by different authorities. According to Schmidt it is due to the action of an enzyme—*fibrin-ferment,* produced probably by the destruction of the white corpuscles, upon the fibrinogen. Another view attributes to the separation of calcium phosphate a large share in the process (Freund), while a third assigns oxidation as the chief cause. The last theory has not received much support.

The solid portion of coagulated blood consists chiefly of red and white corpuscles entangled in a net-work of fibrin.

The *red corpuscles* consist usually of circular, biconcave discs. In birds, amphibia, fishes, and some few mammals, *e.g.*, the camel, they are elliptical and biconvex. Their size varies considerably in different animals, being largest in the amphibia. In man they have an average diameter of ·007 to ·008mm. (=about $\frac{1}{3200}$ inch) and a maximum thickness of ·0019mm. They are heavier than the plasma, having a specific gravity of about 1·09.

The average number in the blood of man is about 5,000,000, in that of woman about 4,000,000, per cubic millimetre. By treatment with water, ether, or other substances, blood corpuscles lose their colouring matter and leave a residue known as the *stroma* of the red corpuscles. This consists of nitrogenous matter and often retains the form of the original corpuscles.

The colour of blood depends upon *hæmoglobin* and its compound with oxygen—*oxyhæmoglobin.* Hæmoglobin consists largely of albumin (about 96 %), the other characteristic component being a colouring matter known as *hæmochromogen* (about 4 %), containing iron.

Hæmoglobin from different animals differs somewhat in composition. Hammarsten gives the following analyses :—

Source.	Carbon.	Hydrogen.	Nitrogen.	Sulphur.	Iron.	Oxygen.
Dog ...	53·85	7·32	16·17	0·390	0·430	21·840
Horse...	54·87	6·97	17·31	0·650	0·470	19·730
Ox ...	54·66	7·25	17·70	0·477	0·400	19·543
Pig ...	54·71	7·38	17·43	0·479	0·399	19·602

It has been calculated that the molecular weight of hæmoglobin must be about 14,000, and a formula which would represent the composition of hæmoglobin from the dog has been given as $C_{636}H_{1025}N_{164}FeS_{8}O_{181}$. Hæmoglobin has the power of uniting with oxygen, with carbon monoxide, or nitric oxide. The stability of the compounds is in the order named and each compound appears to be composed of one molecule of hæmoglobin with one of the gas.

Oxyhæmoglobin is readily obtained in crystals of a bright red colour and soluble in water. It appears to act as a weak acid. A dilute solution shows a characteristic absorption spectrum, containing two chief dark bands, one on the Fraunhofer line D and the other near E.

By the action of reducing agents (*e.g.*, ammoniacal ferrous tartrate), or by the passage of an indifferent gas, or even by exposure in a vacuum, oxyhæmoglobin is deprived of oxygen and *hæmoglobin* is produced. This is darker and more purple in colour and more soluble in water. It readily absorbs oxygen again from the air.

By the decomposition of hæmoglobin a colouring substance named *hæmochromogen* is obtained, which, by oxidation, becomes *hæmatin.* This last substance is said to have the composition $C_{34}H_{35}N_4FeO_5$, and is a dark brown or black solid insoluble in water, acids, alcohol, or ether, but easily soluble in alkalies. By concentrated sulphuric acid, hæmatin is converted, with removal of iron, into a purple red substance known as *hæmato-porphyrin,* said to be $C_{16}H_{18}N_2O_3$.

In addition to the red corpuscles, blood contains *colourless corpuscles* or *leucocytes.* These are of lower specific gravity than the red corpuscles, more variable in size and form, and much less numerous, the relative numbers being one colourless corpuscle to 300 or 500 red ones. They consist of fragments of protoplasm and contain several albuminoids, glycogen or animal starch, lecithin, and cholesterol.

Blood plays an important part in the process of respiration. It is through the blood that the animal organism receives the oxygen so essential for the vital function.

When blood is placed *in vacuo* gases are given off, their composition and amount varying considerably according to the particular part of the body from which the sample was collected. The following table represents the average gaseous contents of arterial and venous blood. 100 volumes of blood yield—

	Arterial blood.	Venous blood.
Oxygen	20	8 to 12
Nitrogen and argon ...	1 to 2	1 to 2
Carbon dioxide ...	40	46

The nitrogen and argon are simply in solution in the blood just as they would be in water; but in the case of oxygen and carbon dioxide the quantity present is much greater than can be explained by simple solution.

In the case of oxygen, for example, the amount present does not vary appreciably with the pressure of the gas in the lungs, whereas the amount of a gas dissolved by a liquid is directly proportional to the pressure of the gas. The greater portion of the oxygen (probably all but about one volume per 100 volumes of blood) is in the state of combination with hæmoglobin. The oxyhæmoglobin is, however, easily dissociated, and if the quantity of dissolved oxygen be diminished from any cause the combined oxygen is diminished proportionately. The great bulk of the oxygen of the blood is thus to be found in the red corpuscles, while only a small quantity is in the plasma.

With carbon dioxide the case is different. Of the 40 to 46 volumes of the gas present in 100 volumes of blood about two are in the state of simple solution, the remainder in a state of weak combination, partly with the hæmoglobin of the red corpuscles, but mainly as bicarbonates in solution in the plasma.

Respiration consists in bringing air into close proximity to the blood stream in the lungs, separation being only maintained by the thin walls of the capillaries and air cells or alveoli. The air in the alveoli is not renewed by mechanical expulsion due to inspiration and expiration, but by diffusion from and into the bronchial tubes.

The partial pressure of the dissolved carbon dioxide in the venous blood is greater than that in the air of the alveoli; consequently the blood plasma loses carbon dioxide, thus producing dissociation of the bicarbonates in solution. The partial pressure of the dissolved oxygen in the venous blood is, however, less than that of the alveolar air, and consequently the plasma takes in oxygen. This disturbs the equilibrium between the dissolved oxygen of the blood plasma and the combined oxygen of the oxyhæmoglobin, causing the formation of more of the latter with a simultaneous diminution of the former. The blood plasma is thus able to take in a further quantity of oxygen from the air. In this way it is probable that all the oxygen which goes into the blood in the lungs does so by passing through the stage of dissolved oxygen in the plasma.

At the same time the air in the lungs becomes saturated with aqueous vapour at the temperature of the body.

The number of respirations per minute varies with the age, &c., of the animal. For adult animals the following is the average :—

Horse	...	9—12
Ox	...	15—18
Sheep	...	13—16

The change produced in the composition of air by respiration is indicated in the following table, which gives the average composition of air before and after inspiration :—

		Inspired air.	Expired air.
Oxygen	...	21·00	16·50
Nitrogen	...	78·03	78·03
Carbon dioxide	...	·03	4·43
Argon, neon, &c.	...	0·97	0·97
Water vapour	...	variable	saturated
Temperature	...	variable	about 36° C.

The most important changes undergone by the air are the loss of oxygen and the gain in carbon dioxide and aqueous vapour. Oxygen by its union with carbon gives rise to its own volume of carbon dioxide. The increase in the volume of carbon dioxide during respiration is, however, almost always less than the decrease in that of oxygen. The quotient $\frac{CO_2 \text{ evolved}}{O_2 \text{ absorbed}}$ is known as the *respiratory quotient*. It varies with circumstances, particularly the food and the amount of muscular exertion. It is usually about ·9. The disappearance of oxygen is probably due to its being used to oxidise hydrogen to water (say from fats and proteids in the food), and also in the formation of certain waste products, *e.g.*, urea.

Seat of oxidation in the body.—Although almost all the oxygen absorption of the body occurs in the lungs (a small amount also through the skin), the act of union with the combustible matter derived from the food and the consequent heat production do not occur there. It is not in the lungs nor even in the blood that the combustion and formation of carbon dioxide occur, but in the tissues themselves.

Bones.—Bone consists mainly of an earthy substance permeated by an albuminoid known as *ossein.* Bones are also intersected by blood-vessels, nerves, &c. The *marrow* of bones contains mainly fat and albumin.

The proportion between the organic matter of bone and its mineral constituents is liable to considerable variation according to the quantities of blood-vessels, nerves, marrow, and water which may be present.

Usually from 30 to 50% of the weight of bone is lost on burning.

The inorganic matter left as ash consists mainly of calcium phosphate, but includes also carbonates, chlorides, and fluorides of calcium and magnesium.

The following table gives the percentage composition of the ash of bones of various animals*:—

	Man.	Ox.	Guinea-pig.
Calcium phosphate ...	83·9	86·0	87·4
Magnesium phosphate ...	1·0	1·0	1·1
Calcium as carbonate, chloride, and fluoride	7·6	7·3	7·0
Carbon dioxide ...	5·7	6·2	—
Chlorine	·2	·2	·1
Fluorine	·2	·3	—
	98·6	101·0	

The proportions of valuable manurial substances in bones has already been given.†

The Fatty Tissue.—This consists of cells, the walls of which are composed of a proteid substance resembling elastin, filled with fat which, during life, is in the fluid state. The fat consists mainly of glyceryl esters of stearic, oleic, palmitic, and other fatty acids; but, in addition, free fatty acids are present in small amount. Animal fats resemble in constitution the vegetable oils already described.*

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* Hammarsten, Physiological Chemistry, 239.

† *v.* p. 135.

Fats from different animals, or even from different parts of the same animal, have very different properties, especially as to consistency and melting point. These depend upon the relative amount of the glycerides of high melting point (*e.g.*, stearin, melting point about 63°, and palmitin, melting point 62°), and those of low melting point (olein, melting point about $-5°$).

The average proportions of fat, water, and membrane (cell walls, &c.) are given by Hammarsten as follows:—

	Water.	Membrane.	Fat.
Fatty tissue of oxen ...	9·96	1·16	88·88
,, ,, sheep ...	10·48	1·64	87·88
,, ,, pigs ...	6·44	1·35	92·21

Fat may be produced in the animal from the fat contained in the food or from proteids or carbohydrates. It forms a valuable reserve from which the animal can draw in times of scarcity of food, being the most concentrated form in which energy can be stored in the animal.

Muscle—Muscular fibre consists of a sheath composed of elastin and the contents, mainly albumins.

Myosin is the principal albuminous constituent of the dead muscle. Its amount varies from 3 to 11%. It is a globulin, is soluble in neutral salt solutions, and coagulates at 56°.

Other albuminoids are found in muscle, of which musculin, muscle-stroma, and myoglobin are the chief.

There are also "nitrogenous extractives" present, the chief being creatin (methyl-guanidine acetic acid), $NH:C(NH_2).N(CH_3).CH_2.COOH+H_2O$; hypoxanthin or sarcin, $C_5H_4N_4O$; xanthin, $C_5H_4N_4O_2$; guanin, $C_5H_5N_5O$; and carnin, $C_7H_8N_4O_3+H_2O$.

Muscle also contains inosit, $C_6H_{12}O_6+H_2O$ (hexahydroxy-hexamethylene), glycogen, $C_6H_{10}O_5$, a sugar (probably glucose and most likely formed after death from glycogen), and sarco-lactic acid, $CH_3.CH(OH).COOH$.

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* *v.* p. 202.

Fat is also present, together with lecithin.

The gases present in muscle consist mainly of carbon dioxide and traces of nitrogen.

Of the *mineral constituents* potassium and phosphoric acid are the chief; sodium, magnesium, calcium, chlorine, and iron are also present. Sulphates are found in the ash, but probably are derived from the sulphur of the proteids.

Detailed analyses of muscle are rarely made, most published analyses having for their object the determination of the nutritive value rather than the true composition.

The following analyses are quoted by Hammarsten :—

	Muscle from mammalians.	Birds.	Cold-blooded animals.
Solids ...	21·7 to 25·5	22·7 to 28·2	20·0
Water ...	74·5 to 78·3	71·7 to 77·3	80·0
Myosin ...	3·5 to 10·6	2·98 to 11·1	2·97 to 8·7
Stroma ...	7·8 to 16·1	8·8 to 18·4	7·0 to 12·1
Alkali-albuminate	2·9 to 3·0	—	—
Creatin ...	·2	3·4	2·3
Xanthin bodies...	·04 to ·07	·07 to ·13	—
Inosit ...	·003	—	—
Glycogen ...	·4 to ·5	—	·3 to ·5
Lactic acid ...	·04 to ·07	—	—

—and a very variable amount of fat.

Living muscle has an alkaline reaction, but after death a change occurs, and it acquires an acid reaction, due probably to the formation of sarcolactic acid.

When muscle contracts oxidation goes on at an accelerated rate and more carbon dioxide is produced and carried away in the blood which bathes the muscle. The consequent increased production of heat is consumed partly in doing the mechanical work performed by the muscle and partly in raising the temperature.

The glycogen and sugar are the chief sources from which this energy is derived. Fat may be consumed if the carbohydrates are in insufficient quantity; but although early experimenters concluded that muscular exertion increased the quantity of nitrogenous waste from the body, more recent researches tend to show that this is not the case. The nitrogenous waste is chiefly excreted in the form of urea in the urine and sweat.

Connective Tissue.—This material, which constitutes the main ingredient in the tendons, ligaments, cartilages, skin, &c., of the animal body, consists essentially of gelatine-yielding substances, of which the following are the chief:—

(1) *Elastin*, an insoluble substance containing little or no sulphur. Its composition, according to analyses quoted by Hammarsten, is about—

Carbon.	Hydrogen.	Nitrogen.	Oxygen.
54·3	7·2	16·7	21·8%

(2) *Collagen*, an insoluble body yielding gelatine by long boiling with water. It contains about ·6% sulphur. Hammarsten gives the following:—

	Carbon.	Hydrogen.	Nitrogen.	Oxygen and sulphur.
Collagen ...	50·75	6·47	17·86	24·92%
Gelatine ...	50·00	6·50	17·50	26·00%

On decomposition it yields albuminous substances and a large quantity of glycocoll [amido-acetic acid, $CH_2(NH_2).COOH$], sometimes called sugar of glue.

(3) *Keratin*.—This is the chief constituent of horns, hoofs, skin, feathers, hair, wool, nails, &c. Obtained from different sources it shows a variation in composition; in general it resembles collagen or gelatine, but differs from those substances in containing much more sulphur (4 or 5%), part of which is in a very loose state of combination and may be removed by alkalies or even by boiling with water. Keratin is insoluble in water, alcohol, or ether, but can be dissolved by heating with water to 150° or 200° under pressure.

DIGESTION.—The food of an animal is rarely in a form capable of direct absorption into the system. Before it can be taken into the blood stream and utilised in the body it is usually necessary that certain chemical changes should be produced so as to render its constituents soluble and diffusible.

These changes are brought about by the process of digestion, which consists mainly in breaking down insoluble, complex carbon compounds into simpler soluble substances, chiefly by the aid of enzymes or unorganised ferments. Digestion is accomplished partly by mechanical, partly by chemical means.

The process commences with mastication—the food is submitted to a comminuting action by the teeth and tongue and at the same time is mixed with *saliva.* This is a very dilute solution of faint alkaline reaction, containing various substances, secreted by special glands and poured into the mouth. It has been estimated that an ox secretes 112℔. of saliva daily. The results of investigations as to the composition of saliva show it to contain only from ·4 to 1 % of solid matter. In human saliva, potassium thiocyanate is usually present, its average amount being probably about ·01 %.

Alkaline chlorides, phosphates, and sulphates are also present, together with *mucin*, a proteid body of slimy consistency. Of special importance is the characteristic enzyme of the saliva—*ptyalin* or *salivary diastase.* This enzyme, which works most rapidly at about 30° and is destroyed at about 65° or 70°, has powers similar to those of plant diastase, *i.e.*, it converts starch, first into soluble starch, next into dextrin, and finally into maltose. The conversion of the starch of food into sugar is commenced, but not completed, in the mouth.

The food next passes into the stomach, which in ruminating animals is divided into several parts and from which the food can be brought back into the mouth to undergo further mastication ("chewing the cud"). In the stomach *gastric juice* is brought into contact with the food. This is a colourless or slightly yellow liquid secreted in the stomach, containing free hydrochloric acid and chlorides and phosphates of calcium, magnesium, and the alkalies. Its characteristic constituents, however, are the enzymes, *pepsin*, which has the power of converting proteids into albumoses and peptones, thereby rendering them soluble and diffusible, and *rennet* or *chymosin*, which coagulates casein. These enzymes have not been obtained in a pure state and to some extent probably exist as "zymogens," *i.e.*, substances which yield the true enzymes on treatment with an acid.

The composition of the gastric juice of various animals is given by Hammarsten thus :—

	Human, mixed with saliva.	Dog. free from saliva	Sheep.
Water	99·44	97·30	98·62
Solids	·56	2·70	1·38
Organic bodies ...	·32	1·71	·41
Common salt ...	·15	·25	·44
Calcium chloride ...	·01	·06	·01
Potassium chloride ...	·06	·11	·15
Free hydrochloric acid	·02	·31	·12
Phosphates of iron, calcium, and magnesium	·01	·20	·21

How the free hydrochloric acid of the gastric juice is secreted from the alkaline blood is not exactly known. Maly's theory is that the carbon dioxide of the blood sets free minute traces of hydrochloric acid from chlorides, possibly through the intervention of phosphates, thus—

$$Na_2HPO_4 + CO_2 + H_2O = NaHCO_3 + NaH_2PO_4$$
$$NaH_2PO_4 + NaCl = Na_2HPO_4 + HCl$$

—and that the acid so formed diffuses from the blood into the gastric juice, being possibly held there in weak combination with pepsin.

Pepsin is apparently a nitrogenous substance like other enzymes, and is destroyed by boiling, though in the dry state it is said to be able to bear a temperature of over 100° without losing its activity. Its characteristic property is its power of converting, in acid but not in alkaline solutions, albuminous bodies into soluble peptones and albumoses. A solution containing about ·1 to ·3% of hydrochloric acid is most favourable for its action.

The proteid swells up and becomes transparent and finally dissolves. In the case of pepsin from most warm-blooded animals, activity ceases below 3° and is at a maximum about 40°. Salicylic acid and phenol hinder digestion by pepsin, while arsenious acid is said to promote it. By the movements of the walls of the stomach the food is kneaded and incorporated with the gastric juice, the pulpy mass produced being known as *chyme*. The chyme then passes into the intestines. The proteids are the principal constituents of the food affected by the gastric juice, though the melting of the fat and the removal of the cell walls from fatty tissue are important physical changes. In the case of animals fed upon starchy foods, a slight amount of hydrolysis, resulting in the formation of sugar and also of lactic acid, is said to occur in the stomach. The chief effect, however, may be said to be the action on the proteids.

The secretion of the glands of the intestines has a strong alkaline reaction and thus tends to neutralise the acidity of the chyme. It has also the property of inverting cane sugar and maltose. The secretions of the pancreas and the liver are next brought into contact with the chyme.

Pancreatic juice is a viscid liquid of alkaline reaction containing albumin, fat, soaps, alkaline carbonates, phosphates, lime, magnesia, and iron. Its characteristic constituents, however, are three enzymes—a diastatic one, a fat-splitting one, and a proteolytic one.

The composition of pancreatic juice appears to be very variable; the amount of total solids, for example, has been observed to vary from 1·5 to 11·5%.

Hammarsten states that the solid matter in the pancreatic juice of the horse varies from ·9 to 1·8%, in that of the sheep from 1·4 to 3·7%, and of the rabbit from 1·1 to 2·6%, and in that of man it is about 2·4%.

The amount of ash, chiefly common salt, appears to be generally from ·6 to ·8%.

The most important constituents are, of course, the enzymes.

(1) The *pancreatic diastase* or *amylopsin*.—This body is similar in many respects to ptyalin, but appears to be distinct from it. It acts upon starch more energetically, even attacking and dissolving unboiled starch. It yields dextrin and maltose.

(2) The *fat-splitting enzyme*, *steapsin*, or *pialyn*.—This enzyme has the power of hydrolysing the fats, *i.e.*, decomposing them into glycerol and free fatty acids, which, in the alkaline liquid, probably form soaps, and at the same time of emulsifying them.

The hydrolytic process only affects a very small amount of the fats; but the emulsification extends to nearly the whole quantity present, the soaps formed in the first process greatly facilitating the formation of the emulsion.

(3) The *proteolytic enzyme, trypsin.*—This acts, like pepsin, in digesting proteids; it differs from the ferment of the gastric juice, however, in acting best in an alkaline solution, and in being more rapid in its action, especially towards fibrin and elastin. In the pancreas itself little or no trypsin exists, but a *zymogen* known as *trypsinogen* occurs. This body, by the action of acids, water, alcohol, or by the natural process of secretion, splits off trypsin.

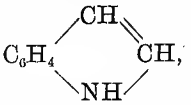
There is some evidence of the existence of a milk-curdling ferment in the pancreatic juice.

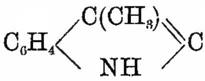
Among the organic constituents of pancreatic juice two substances may be mentioned which are formed in the pancreatic digestion of proteids. These are *leucin*—amido-caproic acid—$CH_3.(CH_2)_3CH(NH_2).COOH$ [or according to Fischer, α-amido-isobutyl acetic acid, $(CH_3)_2CH.CH_2.CH(NH_2).COOH$] and *tyrosin*—para-oxyphenyl amido-propionic acid—$HO.C_6H_4.CH_2.CH(NH_2).COOH$.

They are crystalline compounds, the former very soluble, the latter only slightly soluble, in water. They are both readily soluble in acids or alkalies.

Changes in the Intestines.—As already stated, the intestinal secretions are alkaline, and in such a medium bacteria can readily flourish. Bacteria therefore are usually abundant after the food has passed out of the range of the antiseptic gastric juice. Bacteria effect various changes of a putrefactive character. Carbohydrates undergo the lactic fermentation, cellulose is split up into carbon dioxide and methane, while butyric acid and even free hydrogen are also produced. Other bacteria produce hydrolysis of fats, yielding valeric acid, $C_4H_9.COOH$, or isobutyric acid, $C_3H_7COOH = CH(CH_3)_2.COOH$.

Other microbes act upon the proteids, producing fatty acids and amido-acids, also bodies of the aromatic series, of which indol, skatol, tyrosin, and phenol may be mentioned.

Indol,  $C_6H_4\left\langle\begin{matrix}CH\\NH\end{matrix}\right\rangle CH$, is a crystalline substance melting at 52°, soluble in hot water, very soluble in alcohol or ether. It has a peculiar odour and acts as a weak base. It is found associated with skatol in fæces. It gives a characteristic red precipitate with nitric acid.

Skatol, methyl indol,  $C_6H_4\left\langle\begin{matrix}C(CH_3)\\NH\end{matrix}\right\rangle CH$, also a crystalline body, melts at 95°. It is slightly soluble in water and readily soluble in alcohol, ether, &c. It, like indol, is volatile in steam. It has a most disagreeable fæcal smell. With nitric acid it gives a white precipitate.

Phenol, C_6H_5OH, and *Para-cresol*, $C_6H_4(CH_3)OH$, have also been detected in fæces and result from bacterial action in the intestines.

The Bile.—This product is to be regarded both as a secretion and an excretion of the liver. It is continuously poured into the intestines, though the rate of its discharge varies with circumstances. A reserve is usually stored in the gall bladder, with which many animals are provided.

According to a table given by Gamgee, the amount of bile and bile solids (in grammes) secreted per 24 hours per kilogram of body weight in the case of different animals is as follows:—

	Cat.	Dog.	Sheep.	Rabbit.	Guinea-pig.	Man.
Fresh bile	14·50	19·99	25·41	136·84	175·84	8 to 17
Bile solids	0·82	0·99	1·34	2·47	2·20	0·19 to 0·28

The liver is characterised by containing *glycogen*, $C_6H_{10}O_5$, which may be regarded as a reserve nutritive material. Its amount in the liver varies considerably, being greatly increased after the consumption of food rich in carbohydrates, sometimes rising to 10 or 12%; normally, however, it is probably between 1 and 4%. It disappears during starvation. It is an amorphous, white, tasteless powder.

Bile is a reddish yellow (especially in carnivorous animals) or green (in herbivora) fluid, with faint alkaline reaction and bitter taste. That found in the gall bladder is more concentrated than that obtained directly from the liver. Bile contains sodium and potassium salts of the so-called *bile acids*, *mucin*, or other albumin (to which its viscidity is due), *bile pigments*, *lecithin*, *cholesterin*, *fats*, *soaps*, and *mineral matter*.

The *bile acids* are chiefly *glycocholic acid*, $C_{26}H_{43}NO_6$, and *taurocholic acid*, $C_{26}H_{45}NO_7S$. These are both monobasic acids and give with strong sulphuric acid and cane sugar (or better with a minute trace of furfurol) characteristic colour reactions (Pettenkofer's reaction). The liquid becomes successively cherry red, dark red, and finally purple violet. The acids and their alkaline salts have a strong bitter taste. Solutions of sodium or potassium salts of both acids have solvent powers for soaps, lecithin, and cholesterin.

The acids undergo hydrolysis, taurocholic acid the more readily, yielding, in the one case, *glycocoll* and *cholalic acid*, and in the other, *taurine* and cholalic acid, thus:—

$$C_{26}H_{43}NO_6 + H_2O = CH_2(NH_2)COOH + C_{24}H_{40}O_5$$

and $C_{26}H_{45}NO_7S + H_2O = CH_2(NH_2).CH_2.SO_2.OH + C_{24}H_{40}O_5$.

Glycocoll—glycocine—amido-acetic acid—"sugar of glue," $CH_2(NH_2).COOH$, is a crystalline body, of sweet taste, very soluble in water, and of acid reaction. It is also produced by the decomposition of hippuric acid, $C_6H_6.CO.NH.CH_2.COOH$, and in the pancreatic digestion of gelatine

Taurine, amido-ethyl sulphonic acid, $NH_2.CH_2.CH_2.SO_2.OH$, is a crystalline, tasteless body, soluble in water, insoluble in alcohol, and of neutral reaction.

Cholalic acid, $C_{24}H_{40}O_5$, a monobasic acid, is very slightly soluble in cold water. It has the characteristic bitter taste of the bile acids.

The *bile pigments* are chiefly *bilirubin* and *biliverdin*.

These pigments appear to be formed from hæmoglobin, or rather hæmatin, but contain no iron.

Bilirubin, $C_{16}H_{18}N_2O_3$, is a reddish yellow substance, insoluble in water but soluble in alcohol or chloroform. It is also soluble in alkalies. It is found in bile, especially in that of the carnivora, and also occurs, in combination with calcium, in gall-stones. On exposure to air, alkaline solutions absorb oxygen and become green (biliverdin).

Biliverdin, $C_{16}H_{18}N_2O_4$, is an amorphous green substance, insoluble in water but soluble in alcohol and in alkalies. It is found in bile, in shells of birds' eggs, and sometimes in gall-stones. Other colouring substances have been found in bile.

The *mineral matters* include potassium, sodium, calcium, magnesium, iron, and often traces of copper and zinc; phosphates and chlorides are also present.

Bile undoubtedly plays an important part in the digestion of fats. If the bile be prevented from entering the alimentary canal the fæces become light-coloured, much more putrescent, and contain a large amount of fat. Bile has a slight solvent power upon fats, as is evidenced by the well-known use of ox-gall for removing greasy stains from textile fabrics. It also possesses, in a well-marked degree, the property of aiding the pancreatic juice in bringing about the emulsification of fats; this is probably by virtue of its alkalinity and the power possessed by bile acids and their salts of dissolving lime soap and cholesterin. Bile is said to be possessed of antiseptic properties and to regulate the putrefaction which occurs in the intestines. It is also a laxative.

Bile is to a large extent reabsorbed in the intestines and only a portion is expelled in the fæces.

The Fæces of an animal contain the undigested portions of its food, together with the products of their decomposition under the influence of the enzymes and bacteria present in the alimentary canal, and some portions of the digestive fluids themselves; mucus and epithelial cells from the walls of the intestines are also present.

Small quantities of fat, cholesterin, and calcium and magnesium salts of fatty acids also occur, while the specific odour is due to the presence of skatol and indol or their derivatives, though sometimes sulphuretted hydrogen, ammonia, amines, and other volatile substances are present. A dark brown reduction product of bilirubin known as *hydro-bilirubin*, $C_{32}H_{40}N_4O_7$, is said to be often present.

Absorption of Digested Food.—Water and inorganic compounds, *e.g.*, common salt, are absorbed without change. Little or no absorption takes place in the mouth or gullet. It commences in the stomach, but is mainly accomplished in the intestines. The absorption is not merely a physical process of diffusion; the living cells through which it occurs exercise a selective action and in many cases produce important chemical changes in the substance being absorbed.

Absorption of carbohydrates.—These are probably entirely absorbed as glucose, the necessary changes being produced in the food by the enzymes in the saliva, pancreatic juice, and intestine as already described. A portion at once enters the blood stream and is conveyed to the tissues, while another portion is probably stored as a reserve in the liver in the form of glycogen.

Absorption of fats.—A small portion of the fat in the food is saponified; but, as already stated, the greater portion is merely emulsified. The lacteals of the intestine are the absorbents for fat, and exactly how the minute globules pass through the walls of the intestine is not understood. When fatty acids are fed to an animal the contents of the lacteals contain fat, so that glycerine must have come from some other portion of the food and fat must be synthesised.

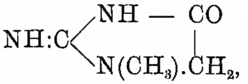
Absorption of proteids.—Soluble proteids are often absorbed unchanged; in general, however, the proteids are converted into peptones and albumoses by the action of either pepsin or trypsin. The extraordinary fact is that in the blood no peptones can be found; indeed, if they be injected into the blood stream, poisonous effects are at once produced. The epithelial cells must, during absorption, change the peptones and albumoses back again into the original proteids.

The length of the alimentary canal varies greatly in different animals, being comparatively short in carnivora and very long in herbivora. The usual length of the intestines of the various farm animals and the percentage ratio of the capacity of the stomach to the total capacity of stomach and intestines are as follows:—

	Length of intestines in feet.	Ratio of capacity of stomach. %
Horse ...	98	8·5
Ox ...	187	71·0
Sheep ...	107	67·0
Pig ...	77	29·0

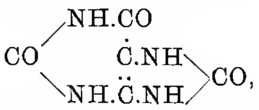
The Urine.—This is, perhaps, the most important excretion of the animal body, since in it are the nitrogenous waste products, the water and the soluble mineral salts derived from the food or the breaking down of tissue. It is formed (or, probably more correctly, extracted) from the blood by the kidneys, which contain several albuminous bodies, fat, xanthin, urea, uric acid, glycogen, leucin, inosit, taurin, and cystin. The last-named substance has the composition $C_6H_{12}N_2S_2O_4$. Urine varies greatly in composition with the breed of animal, the food, quantity of exercise, amount of water taken, and many other circumstances. In carnivora and man, urine is usually acid, while in herbivora it is neutral or alkaline.

The specific gravity varies greatly; its determination furnishes an important means of estimating the total solids present. In the case of human urine, variations from 1·002 to 1·040 have been observed. The characteristic constituent of urine is *urea* or *carbamide*, $CO(NH_2)_2$, which is more abundant in the urine of carnivora than in that of herbivora.

Creatinin, $C_4H_7N_3O$, or 

$$NH{:}C\begin{array}{l} NH - CO \\ \qquad\quad\ \, | \\ N(CH_3).CH_2, \end{array}$$

xanthin, $C_5H_4N_4O_2$, and smaller quantities of allied substances also occur in the urine of man and some mammalia.

Uric acid, $C_5H_4N_4O_3$, or 

$$CO\begin{array}{l} NH.CO \\ \qquad\ \ C.NH \\ NH.C.NH \end{array}\!\!>CO,$$

occurs abundantly in the excrements of birds and serpents, also in the urine of carnivora and man, and, to a very small extent, in that of the herbivora. Uric acid is a dibasic acid, and both the acid and its acid salts are very slightly soluble in water. In certain diseases, *e.g.*, gout, deposits of uric acid and urates are formed in the body.

Hippuric acid, benzoylamido-acetic acid, $C_9H_9NO_3$, or $C_6H_5.CO.NH.CH_2.COOH$. This substance is found (to the amount of about 2%) in the urine of horses, cattle, and many herbivora; it is also present in human urine (usually about ·5%), and, during starvation, in that of carnivora.

Hippuric acid readily decomposes (under hydrolysis), giving benzoic acid and amido-acetic acid (glycocoll), $C_6H_5CO.NH.CH_2.COOH+H_2O = C_6H_5.COOH+CH_2(NH_2).COOH$.

It is probably from the phenyl derivatives present in hay, grass, and many fruits and berries that hippuric acid is formed in the animal. Moreover, the putrefaction of proteids yields certain phenyl derivatives which may produce benzoic acid and thus hippuric acid on oxidation.

Other derivatives of benzene occur in the urine, especially of herbivora, thus, *phenyl sulphuric acid,* $C_6H_5.O.SO_2.OH$, occurs as potassium salt. *Cresyl sulphuric acid,* $C_6H_4(CH_3).O.SO_2.OH$, and *pyrocatechin sulphuric acid,* $C_6H_4(OH).O.SO_2.OH$, also occur in the urine of horses. *Indoxyl sulphuric acid,* $C_8H_6N.O.SO_2.OH$, or *indican,* is also found in urine, especially of herbivora. By warming with acids, its potash salt yields *indoxyl* and potassium sulphate—

$$C_8H_6N.O.SO_2.OK+H_2O = C_8H_6N(OH)+KHSO_4.$$

On oxidation, *e.g.*, by bleaching powder, indoxyl yields indigo—

$$2C_8H_6N.OH+O_2 = C_{16}H_{10}N_2O_2+2H_2O.$$

CHAPTER XIII.

FOODS AND FEEDING.

In previous chapters many references have been made to the chief constituents of the food of animals.

In this chapter will be given a summary of some of the chief facts relating to the composition, digestibility, and other properties of foods, and to the principles upon which the construction of rations or diets for special purposes is based.

The Composition of Foods.—This subject has already been discussed (Chap. IX.). The useful constituents of foods are classed as—

$$\text{1. Non-nitrogenous}\begin{cases}\text{Carbohydrates,}\\ \text{Fat,}\\ \text{Minerals ;}\end{cases}$$

$$\text{2. Nitrogenous}\quad\ldots\begin{cases}\text{Amides,}\\ \text{Albuminoids ;}\end{cases}$$

while in a third class are placed the portions which are thought to be indigestible and comparatively useless—the so-called "crude fibre." Though this method of classification is not entirely satisfactory, it is convenient, especially as the larger number of published analyses are expressed according to it. The more satisfactory plan (possible because of recent improved methods of analysis), in which the carbohydrates are differentiated, has been already alluded to. Unfortunately only a limited number of food stuffs have hitherto been examined by these later methods.

Another improvement in food analysis, not, however, of such recent introduction, is the differentiation of the nitrogenous constituents into amides and albuminoids. In older analyses the total nitrogen of the food was determined, and, multiplied by 6·25, was taken as a measure of the albuminoids.

As already stated, many vegetable products contain a considerable proportion of their nitrogen in the form of amides and in some cases as nitrates. Large numbers of analyses in which the distinction between the nitrogen existing as albuminoids and in other forms has been made are now available*

The composition of the more important crops of the farm has been given on pages 251, 252, and 253.

In addition, certain concentrated foods are employed. Many of these are residues from the manufacture of oil from seeds,† known as *oil-cakes*, or of flour, &c., from grain. They consist chiefly of the husk and solid portion of the seeds and are usually rich in albuminoids, minerals, and oil. The chief varieties of oil-cake used as food are—

Linseed cake.—The composition of linseed has already been given. In the manufacture of linseed oil the crushed seed is treated by one of two processes—(1) simple pressure aided by heat, or (2) extraction by means of petroleum naphtha. In the latter process, which is largely replacing the older one, especially in America, the solvent is removed by means of steam, and the pressed residue is then ground and sent into the market as oil meal or linseed meal. The new process meal is richer in protein and carbohydrates, but much poorer in fat. It is also less digestible than the old process meal.

Properly ripened linseed is free from starch, though the immature seed contains a small quantity. Many weed seeds, perhaps accidentally mixed with the linseed, usually are rich in starch. As a rule the oil extractor is careful to exclude all foreign matters from the seed because of its retaining the oil, which is very valuable (particularly at present, its price being now [1901] about double its usual one). The presence of starch, therefore, in linseed cake or meal generally indicates adulteration after the extraction of the oil.

Occasionally the husks of the castor-oil seed occur in linseed cakes (probably through accident), and such cakes are often poisonous. A method for the detection of such admixture is described by Leather.‡

As a rule, Russian and English cakes are richest in oil, while the American products excel in nitrogenous compounds. Indian cakes are poorest in albuminoids, and American ones, owing to the higher pressures employed in their manufacture, are deficient in oil.

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* *v.* Chap. XI.

† *v.* Chap. IX., p. 205.

‡ Jour. Roy. Agric. Soc. 1892.

Cotton-seed cake.—For composition of the seed see p. 251. Two varieties of cake are made—*decorticated*, in which the envelopes of the seed, with the adhering particles of cotton, are removed before expressing the oil; and *undecorticated*, in which the whole seed is subjected to hydraulic pressure. The latter is naturally of much less value than the former.

The "hulls" removed in the process of "decortication" are used locally as food for cattle, but in England are not of much importance.

Decorticated cotton cake is a concentrated and valuable food for all farm animals except pigs and calves. In the case of the animals mentioned sickness and death have frequently resulted from feeding with cotton cake or meal. The cause of the poisonous effect does not appear to be known, though it has been attributed to *choline*, which is present in cotton seed.*

Cotton-seed cake fed to dairy cows increases the firmness and whiteness of the butter, but if used too freely causes the butter to give the reactions for cotton-seed oil, thus giving rise to the suspicion of the butter being adulterated with margarine.

Rape-seed cake.—This product is little used as food, especially in England, owing to its not being very palatable. Its composition, however, shows it to have a high nutritive value. When the oil has been extracted by means of solvents the cake is largely used as a manure.

Earth-nut or pea-nut cake.—This is a valuable food, largely employed on the Continent, though little used in England or America. It is particularly rich in proteids.

Palm-nut cake or meal is also employed on the Continent as a food, being appetising, digestible, and of good keeping property. It is much valued for dairy cows.

Sunflower-seed cake.—Sunflower seed is a valuable crop in certain parts of Russia and contains about 20% of oil. When this is extracted by pressure, the residue, containing from 9 to 14% of oil and from 30 to 45% of albuminoids, is sometimes used as a cattle food.

Corn-oil cake or *germ-oil meal* is the residue left after the extraction (by pressure) of the oil from maize germ. This product is largely produced and used as food in America. It is rich in proteids and fat and very digestible. Attempts have lately been made to introduce this and other maize bye-products into England, particularly for dairy cows.

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* *v.* page 217.

Other important bye-products used as food stuffs are :—

1. From Wheat.

Bran.—This consists of the outer portion of the wheat grain, and though somewhat rich in indigestible fibre is a valuable food because of its albuminoid and fat content. It is also rich in phosphates and potash.

Sharps, *shorts*, and *middlings* are similar to bran, being largely composed of its smaller fragments, together with a portion of the more starchy flour.

Wheat germ, consisting of the embryo, is very rich in oil.

2. From Maize.

Maize bran or fancy corn bran is the husk or hull of Indian corn.

Gluten meal is the highly nitrogenous matter which lies immediately below the husk.

Germ meal or cake is the nitrogenous and fatty residue left after expressing the oil from the germ of maize.

These foods, now largely used in America for fattening and milk production, are bye-products in the manufacture of starch and glucose from Indian corn. Several other products of these processes are also employed, *e.g.*, "glucose meal," "sugar meal," "starch refuse," "starch feed," &c.

3. From Barley.

Malt dust or *malt coombs.*—Malt is produced by soaking barley in water and allowing it to germinate on the floor of a suitable building, with repeating turning, until the shoots attain a certain length. The malt is then kiln dried, when the shoots are broken off. The chief changes produced during malting are the growth of the germ; the production of diastase and the consequent production of sugar from a portion of the starch, and the formation of amides from proteids. In drying, though the vitality of the plant is destroyed, care is taken not to kill the diastase, which is required in the subsequent processes of brewing. If, through accident, malt becomes damaged, it is sometimes used whole for feeding purposes. In any case the dried shoots of the barley have to be removed from the malt and constitute "malt coombs." These are rich in nitrogen and mineral matter, and are sometimes used as manure; more generally they are employed, after being soaked in water, as a small ingredient in the food of pigs or cattle.

Brewers' grains.—These consist of the residue left after "mashing" the malt, whereby the greater portion of its carbohydrates are converted into sugar by the diastase and removed in the wort. They are largely employed locally as food for dairy cows and have the reputation of greatly increasing the quantity, while diminishing the quality, of the milk flow. As the wet grains are very liable to undergo fermentation and putrefaction, they are not desirable as food for milk-cows, unless the greatest cleanliness and care be taken in supplying them. Otherwise, there appears to be little objection to their use.

Dried grains.—Grains direct from the brewery contain too much water and are too liable to change to permit of their being used except in the immediate neighbourhood. In order to render them more portable they are sometimes dried and then furnish a valuable food.

4. From Oats.—As a rule, oats are employed, either whole or crushed, as food, mainly for horses, though dairy cows are sometimes fed with oats in Denmark. New oats are not suited to working horses, though what change they undergo on keeping is not known.

The bye-products in the manufacture of oatmeal are comparatively worthless, the husk or hull being mainly "crude fibre."

5. From Rice.

Rice meal is really rice bran and comprises the outer layer of the grain, together with a portion of the germ. It is rich in nitrogenous matter, fat, and ash constituents.

Rice polish, a fine powder, is a still more highly nitrogenous food, and is very rich in phosphoric acid.

In addition to those mentioned, certain other bye-products are sometimes used as food. Their composition will be seen from the table.

The value of a food depends partly upon its composition, partly upon its digestibility.

In order to determine the latter, which varies considerably with different races of animals and also in different individuals of the same race, food of known composition is supplied in known quantities to animals and their solid excrements collected, weighed, and analysed. In this way the amounts of the various constituents which have been assimilated can be ascertained; errors, which are generally slight, but which in certain cases may be considerable, are introduced by the admixture of intestinal secretions, bile, &c., with the fæces. These secretions increase the nitrogenous and fatty constituents of the excrements, and therefore tend to give too low values for the digestibility of the proteids and fats.

The proportion of each food constituent digested out of 100 supplied is known as the "*digestion coefficient.*"

In the tables are given the digestion coefficients of the constituents of a large number of food stuffs, chiefly from the results of American and German experiments. It is to be noted that by "digestibility" of a food or constituent of a food no reference is paid to the rapidity or ease with which it is assimilated, nor to the effect upon the health or comfort of the animal consuming it. These are points on which the taste and individuality of the animal have even more influence than on the true digestibility, *i.e.*, the actual chemical transformations leading to the assimilation.

In America attempts are being made to distinguish between *digestibility* and *availability* of the constituents of food. As defined by Atwater,* these are—

Digestibility:—Measured by the difference between the total food and the undigested residue.

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* Rep. of Storr's Agric. Expt. Station, 1899, 69.

Availability:—Measured by the difference between the total food and the fæces.

The former is almost impossible to determine, because of the difficulty of distinguishing between the undigested residue of the food and the matter which is derived from the digestive fluids.

AVERAGE DIGESTION COEFFICIENTS IN VARIOUS FOODS.

I.—*For Ruminants.*

	Protein.	Carbo-hydrates.*	Fat.	Crude fibre.	Total dry matter.
Maize	76	93	86	58	91
Gluten meal	89	93	93	—	88
Gluten feed	85	87	83	72	84
Wheat bran	79	69	68	22	61
Wheat sharps	82	85	85	36	79
Rye meal	84	92	64	—	87
Barley	70	92	89	50	86
Malt sprouts or coombs...	80	69	100	34	67
Brewers' grains, wet ...	73	62	86	40	63
,, ,, dried ...	79	59	91	53	62
Oats	78	76	83	20	70
Rice meal	63	86	85	26	75
Linseed	91	55	86	61	77
Linseed meal, rich in oil	89	78	89	57	79
,, ,, poor in oil	85	84	93	74	80
Cotton seed	68	50	87	76	66
Cotton cake, decorticated	88	64	93	32	76
,, ,, undecorticated	62	54	85	46	55
Pea meal	83	73	85	—	79
Meadow hay	57	64	53	60	61
Timothy hay	48	63	57	52	57
Red clover hay ...	62	69	62	49	61
Alsike hay	66	71	50	53	62
White clover hay ...	73	70	51	61	66
Lucerne hay	74	66	39	43	60

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* According to experiments with sheep by Fraps (Journal of Amer. Chem. Soc. 1900, 543; Jour. Soc. Chem. Ind. 1900, 1030), sugars are completely digestible, while pentosans, on the average, have a digestion coefficient of 64·3. The order of digestibility of non-nitrogenous food constituents is (1) sugar, (2) starch, (3) pentosans, (4) residue ("crude fibre").

	Protein.	Carbo-hydrates.	Fat.	Crude fibre.	Total dry matter.
Sainfoin hay	70	74	66	36	62
Wheat straw	11	38	31	52	43
Rye straw	21	37	32	60	46
Oat straw	30	44	33	54	48
Barley straw	20	54	42	56	53
Pasture grass, green	70	73	63	76	71
Timothy grass, green	50	64	47	52	58
Green oats, in bloom	75	63	70	60	64
Red clover, green	67	78	65	53	66
Crimson clover, green	77	74	66	56	69
Lucerne, green	81	76	52	45	67
Potatoes	61	90	—	—	85
Mangolds	77	96	—	—	88
Turnips	90	97	98	100	93
Swedes	80	95	84	74	87
Cows' milk	94	98	100	—	98
II.—*For Pigs.*					
Maize meal	86	95	76	40	92
Pea meal	89	95	50	78	90
Barley meal	76	90	65	15	82
Wheat	70	74	60	30	72
Wheat bran	75	66	72	34	61
Wheat sharps	73	87	—	37	77
Potatoes	73	98	—	55	93
Dried blood	72	92	—	—	72
Flesh meal	97	—	87	—	92
Sour milk	96	99	95	—	95

Pigs have the power of digesting large proportions of highly concentrated foods, but the shortness of their digestive canals seriously lessens the amounts of "crude fibre" and of bulky fodder which they can digest.

Horses show similar inferiority in digestive power when compared with ruminants. With protein, however, they are practically as well able to deal; but with carbohydrates, fats, and fibre they are distinctly inferior to sheep.

The quantity of food supplied to an animal has little influence on the proportion digested unless the diet is very rich and generous; the digestibility of the food then diminishes.

From the laborious investigations of Grandeau and his associates it appears that gentle exercise increases the proportion of food digested by horses, while work slightly diminishes it.

Fodder is subject to the greatest variation in digestibility, being almost always most digestible when young. This is true, manifestly, with reference to the "fibre," which becomes less and less digestible as the plant becomes more lignified, but also applies to the proteids, fat, and starch. This is well seen by reference to the digestion coefficients for hay and green grass, clover, &c., in the table just given.

It is found that the digestibility of some constituents may be altered by the addition to the food of an increased quantity of one constituent. This is only true under certain circumstances, viz., when the *albuminoid ratio* of the food is changed so as to fall outside certain limits, which differ with the particular animal considered. By *albuminoid ratio* or *nutritive ratio* is meant the ratio of the digestible albuminoids to the digestible non-albuminoids expressed in equivalent of starch. The calculation of the starch equivalent of fat, sugar, &c., is based upon the results of calorimetric experiments, *i.e.*, the quantities which will produce by their combustion an equal amount of heat.

By placing an animal in a respiration calorimeter, so arranged that everything which enters and leaves may be measured, the quantities of various dry food stuffs which will produce in the body of the animal as much heat as 100 parts of fat has been determined. The following table gives the results as compared with those obtained by direct oxidation of the food in a combustion calorimeter*:—

	As determined with animals.	As determined in combustion calorimeter.
Myosin	225	213
Lean meat ...	243	235
Starch	232	229
Cane sugar ...	234	235
Grape sugar ...	256	255

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* Rubner, quoted by Atwater, Bull. 21 U.S. Dept. of Agriculture. Atwater found, as a mean, that the heats of combustion of the available fat, protein, and carbohydrates of foods were represented by 9400, 4400, and 4100 thermal units (Rep. of the Storrs Agric. Expt. Station, 1899). These numbers agree well with the older numbers obtained by Rubner in 1885.

The agreement between these two sets of numbers is as close as can be expected.

Rubner gives the following as the approximate heats of combustion of the three principal classes of food :—

1 gramme of fat		yields	9300	thermal	units
1 ,,	protein	,,	4100	,,	,,
1 ,,	carbohydrates	,,	4100	,,	,,

—or, in other words, 1 gramme of fat would, by union with oxygen, evolve heat sufficient to raise the temperature of 9300 grammes of water through 1° C., while a gramme of protein or carbohydrates would, on burning, suffice to heat 4100 grammes of water through 1° C. The numbers given are averages, and in any particular case slightly higher or lower values might be obtained.

The ratios of the heat-producing powers of the three food stuffs thus are approximately—

Starch (and other carbohydrates) ...	1
Protein	1
Fat	2·27

—or 1 : 1 : 2·3.

The albuminoid or nutritive ratio of a food is therefore calculated from its *digestible constituents*, thus—

$$\frac{\text{Albuminoids}}{\text{Carbohydrates} + (\text{fat} \times 2{\cdot}3)}.$$

It is found that the nutritive ratio of the food of an animal must not fall outside certain limits (which vary with circumstances) or either its health and condition suffer, or waste of food is entailed. Before discussing the subject further, however, it is advisable to give a table of the *digestible constituents of the important food stuffs.*

Such a table can be calculated from the tables already given, since the two factors governing it are obviously the composition of the foods and the digestibility of their constituents.

The following table, mainly from American and German experiments,* gives the percentage amounts of digestible constituents and of fertilising materials in the more important feeding stuffs :—

DIGESTIBLE AND FERTILISING CONSTITUENTS OF VARIOUS FOOD STUFFS.

		Digestible constituents percentages.			Fertilising constituents percentages.		
Food.	Dry matter per cent.	Protein.	Carbo-hydrates.	Fat.	Potash.	Phosphoric acid.	Nitrogen.
Maize	89·1	7·9	66·7	4·3	0·40	0·70	1·82
Maize bran	90·9	7·4	59·8	4·6	0·68	1·21	1·63
Gluten meal	91·8	25·8	43·3	11·0	0·05	0·33	5·03
Germ meal	89·6	9·0	61·2	6·2	0·50	0·80	2·65
Wheat	89·5	10·2	69·2	1·7	0·50	0·79	2·36
Flour	87·6	8·9	62·4	0·9	0·15	0·22	1·89
Wheat bran	88·1	12·2	39·2	2·7	1·61	2·89	2·67
Sharps or shorts	88·2	12·2	50·0	3·8	0·59	1·35	2·82
Rye	88·4	9·9	67·6	1·1	0·54	0·82	1·76
Rye bran	88·4	11·5	50·3	2·0	1·40	2·28	2·32
Barley	89·1	8·7	65·6	1·6	0·48	0·79	1·51
Malt coombs	89·8	18·6	37·1	1·7	1·63	1·43	3·55
Brewers' grains, wet	24·3	3·9	9·3	1·4	0·05	0·31	0·89
Ditto, dry	91·8	15·7	36·3	5·1	0·09	1·03	3·62
Oats	89·0	9·2	47·3	4·2	0·62	0·82	2·06
Oat meal	92·1	11·5	52·1	5·9	—	—	—
Rice	87·6	4·8	72·2	0·3	0·09	0·18	1·08
Rice bran	90·3	5·3	45·1	7·3	0·24	0·29	0·71
Buckwheat	87·4	7·7	49·2	1·8	0·21	0·44	1·44
Linseed	90·8	20·6	17·1	29·0	1·03	1·39	3 61
Linseed meal, pressure	90·8	29·3	32·7	7·0	1·37	1·66	5·43
Ditto, solvent	89·9	28·2	40·1	2·8	1·39	1·83	5·78
Cotton seed	89·7	12·5	30·0	17·3	1·17	1·27	3·13
Cotton-seed meal	91·8	37·2	16·9	12·2	0·87	2·88	6·79

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* See Henry : Feeds and Feeding, 1898.

Food.	Dry matter per cent.	Digestible constituents percentages.			Fertilising constituents percentages.		
		Protein.	Carbo- hydrates.	Fat.	Potash.	Phosphoric acid.	Nitrogen.
Palm-nut meal	89·6	16·0	52·6	9·0	0·50	1·10	2·69
Sunflower seed	92·5	12·1	20·8	29·0	0·56	1·22	2·28
Sunflower-seed cake ...	91·8	31·2	19·6	12·8	1·17	2·15	5·55
Pea-nut meal ...	89·3	42·9	22·8	6·9	1·50	1·31	7·56
Rape-seed meal	90·0	25·2	23·7	7·5	1·30	2·00	4·96
Peas ...	89·5	16·8	51·8	0·7	0·99	0·82	3·08
Horse beans ...	85·7	22·4	49·3	1·2	1·29	1·20	4·07
Pasture grass ...	20·0	2·5	10·2	0·5	0·75	0·23	0·91
Timothy grass	38·4	1·2	19·1	0·6	0·76	0·26	0·48
Green oats ...	37·8	2·6	18·9	1·0	0·38	0·13	0·49
Meadow fescue	30·1	1·5	16·8	0·4	—	—	—
Green barley ...	21·0	1·9	10·2	0·4	—	—	—
Timothy hay ...	86·8	2·8	43·4	1·4	0·90	0·53	1·26
Mixed grass hay	87·1	5·9	40·9	1·2	1·55	0·27	1·41
Meadow fescue hay ...	80·0	4·2	43·3	1·7	2·10	0·40	0·99
Wheat straw ...	90·4	0·4	36·3	0·4	0·51	0·12	0·59
Rye straw ...	92·9	0·6	40·6	0·4	0·79	0·28	0·46
Oat straw ...	90·8	1·2	38·6	0·8	1·24	0·20	0·62
Barley straw ...	85·8	0·7	41·2	0·6	2·99	0·30	1·31
Red clover, green	29·2	2·9	14·8	0·7	0·46	0·13	0·53
Alsike clover ..	25·2	2·7	13·1	0·6	0·20	0·11	0·44
Crimson clover	19·1	2·4	9·1	0·5	0·49	0·13	0·43
Lucerne ...	28·2	3·9	12·7	0·5	0·56	0·13	0·73
Red clover hay	84·7	6·8	35·8	1·7	2·20	0·38	2·07
Alsike ditto ...	90·3	8·4	42·5	1·5	2·23	0·67	2·34
White ditto ...	90·3	11·5	42·2	1·5	1·81	0·52	2·75
Crimson ditto ...	90·4	10·5	34·9	1·2	1·31	0·40	2·05
Lucerne hay ...	91·6	11·0	39·6	1·2	1·68	0·51	2·19
Clover silage ...	28·0	2·0	13·5	1·0	—	—	—
Lucerne ditto ...	27·5	3·0	8·5	1·9	—	—	—

Food.	Dry matter per cent.	Digestible constituents percentages.			Fertilising constituents percentages.		
		Protein.	Carbohydrates.	Fat.	Potash.	Phosphoric acid.	Nitrogen.
Grass silage ...	32·0	1·9	13·4	1·6	—	—	—
Maize ditto ...	20·9	0·9	11·3	0·7	0·37	0·11	0·28
Potatoes ...	21·1	0·9	16·3	0·1	0·46	0·12	0·32
Mangolds* ...	9·1	1·1	5·4	0·1	0·38	0·09	0·19
Turnips ...	9·5	1·0	7·2	0·2	0·39	0·10	0·18
Swedes ...	11·4	1·0	8·1	0·2	0·49	0·12	0·19
Carrots ...	11·4	0·8	7·8	0·2	0·51	0·09	0·15
Parsnips ...	11·7	1·6	11·2	0·2	0·44	0·20	0·18
Artichokes ...	20·0	2·0	16·8	0·2	0·47	0·14	0·26
Cabbages ...	15·3	1·8	8·2	0·4	0·43	0·11	0·38
Spurrey ...	20·0	1·5	9·8	0·3	0·59	0·25	0·38
Prickly comfrey	11·6	1·4	4·6	0·2	0·75	0·11	0·42
Rape ...	14·0	1·5	8·1	0·2	0·36	0·15	0·45
Acorns, fresh ...	44·7	2·1	34·4	1·7	—	—	—
Dried blood ...	91·5	52·3	0·0	2·5	0·77	1·35	13·50
Cows' milk ...	12·8	3·6	4·9	3·7	0·18	0·19	0·53
Separated milk	9·4	2·9	5·2	0·3	0·19	0·20	0·56
Butter milk ...	9·9	3·9	4·0	1·1	0·16	0·17	0·48
Whey ...	6·6	0·8	4·7	0·3	0·18	0·14	0·15

The above table, though useful and perhaps sufficiently accurate for many purposes, is by no means perfect.

In the first place the column headed "protein" includes all the nitrogenous ingredients, both true albuminoids and amides, the amounts being derived from the determination of the total nitrogen. So, too, the item "carbohydrates" is unsatisfactory for the reasons stated in Chapter XI. Another fact to be remembered is our incomplete knowledge of the "digestion coefficients" in any particular case, these being subject to enormous variations with different samples of food and with different animals.

Such tables can therefore be taken only as rough guides in framing rations.

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* English mangolds are usually of better feeding value than either swedes or turnips.

The proportion of the total digestible nitrogenous matter which exists as true albuminoids in the food varies greatly. In concentrated foods, *e.g.*, cakes, grains, &c., it is high, while in hay, grass, and especially roots, it sinks to a very low figure.

Warington* gives the following as the digestible nitrogenous matter and digestible albuminoids present in several food stuffs :—

	Nitrogenous substances. %	True albuminoids. %
Cotton cake (decorticated) ...	39·0	37·2
,, (undecorticated) ...	16·3	14·9
Linseed cake	24·0	22·6
Peas	20·0	17·5
Beans...	22·4	19·6
Wheat	10·2	8·8
Wheat bran	11·0	8·9
Oats	8·9	8·2
Barley	7·4	6·9
Malt dust	19·2	12·1
Brewers' grains (wet) ...	3·7	3·4
,, ,, (dried) ...	14·4	13·2
Maize...	7·9	7·3
Rice meal	7.5	6·5
Pasture grass	2·8	1·8
Clover (green)	2·5	1·7
Clover hay	7·8	5·2
Meadow hay	3·3 to 7·9	2·8 to 6·1
Maize silage	·8	·1
Oat straw	1·6	1·1
Barley straw	·9	·6
Potatoes	1·6	·7
Carrots	·9	·4
Mangolds	·9	·2
Swedes	·9	·2
Turnips	·6	·1

The "nitrogenous substances" or "protein" is calculated from the amount of total nitrogen found on analysis, by assuming that every 1 per cent. of nitrogen corresponds to 6·25 per cent. of protein (*v.* Chap. XI.).

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* Chemistry of the Farm.

In grasses, hay, &c., a large proportion of the total nitrogen exists as amides, of which asparagine, $CONH_2.C_2H_3(NH_2).COOH$ (*v.* p. 217), may be taken as a type.

Amides are usually stated as being used in the body simply as heat producers and to be incapable of acting like albuminoids as flesh formers. Though undoubtedly inferior to albuminoids, it appears from recent experiments that amides do to a certain extent perform the functions of these substances. They certainly lessen the consumption of albuminoids and greatly diminish the waste of nitrogenous tissue when albuminoids are fed in insufficient quantity.* It is therefore not quite satisfactory to disregard the amides of a food, nor even to merely assign to them, as is often done, the functions of heat producers only. From this last aspect asparagine has only about half the value of starch, when due allowance is made for the nitrogen excreted as urea.

In other foods, especially in mangolds, a large proportion of the nitrogen exists as nitrates,† and thus probably is devoid of all feeding properties. In calculating the nutritive ratio of a food, therefore, wherever possible the amount of digestible albuminoids should be used and the amides considered as non-albuminoids and equal to about half their weight of starch.

When this is done it is probable that the calculated "albuminoid ratio" is wider than it should be, especially in cases where much amide is present, *e.g.*, in silage.

The "albuminoid ratio" is obviously not a very constant or reliable number, since it depends not only upon composition but also upon digestibility. Still, it affords a valuable means of classifying rations and has proved of much service in feeding practice.

Calorific Value of Food Stuffs.—The relative values of food stuffs can, to some extent, be assessed from their power of evolving heat when oxidised. If the food of an animal contain sufficient nitrogenous matter to replenish the waste of tissue necessitated by the vital processes, the heat-producing power of the food then becomes a measure of the amount of mechanical work which the animal can perform or of the quantity of heat which the food can supply. These quantities are related to the capacity for producing fat, since fat may be regarded as stored energy. The calorific power of a food, therefore, if calculated from the digestible constituents, affords a fair measure of its feeding power; due attention, however, must be paid to the capability of the food for replenishing waste of tissue (*i.e.*, to its containing a due proportion of albuminoids).

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* Brutskus, Exper. Stat Record 1899, 275; Jour. Chem. Soc. 1900, abst. ii. 237.

† This was strikingly demonstrated by an observation made by the author in 1900 that some pulped mangold kept for some weeks in a stoppered bottle evolved nitric oxide, doubtless as the result of the action of some denitrifying organism upon the nitrates. A similar production of nitric oxide has been noticed from the pulp of the sugar beet.

In such a calculation the heat of combustion of albuminoids, carbohydrates, and fat, already given, may be employed. For example, the heat-yielding power of maize is thus calculated:—

1 gramme of maize contains	·079	digestible	protein
	·667	,,	carbohydrates
	·043	,,	fat.

Multiplying these by their respective heats of combustion—

$$\begin{aligned} \cdot079 \times 4100 &= 324 \text{ calories} \\ \cdot667 \times 4100 &= 2735 \ \ ,, \\ \cdot043 \times 9300 &= 400 \ \ ,, \\ \hline &\quad 3459 \ \ ,, \end{aligned}$$

—or 1 gramme of maize when used as food is theoretically able to produce 3459 units of heat; or, to express it more generally, one part by weight of maize when used as food is able to produce sufficient heat to raise the temperature of 3459 parts by weight of water through one degree Centigrade. In fact, the results obtained by such calculations are really the *calorific powers* of the food stuffs when oxidised in the animal. As would be expected, foods richest in fat are generally of highest calorific power.

The following table gives the approximate fuel values of many of the commoner food stuffs. The numbers are calculated from a table of the digestible ingredients of various foods given in Farmers' Bulletin, No. 22, of the U.S.A. (1895) Dept. of Agriculture. They agree approximately with the figures, calculated in the manner just described, from the table on pp. 288, 289, and 290, though in certain cases discrepancies will be found, owing to different numbers for the digestible constituents being taken.

Substance.	Fuel value of 1 gramme, in calories.
Gluten meal	3750
Maize	3460
Wheat	3420
Cotton-seed meal	3370
Rye	3360
Pea-nut meal	3340
Linseed meal (old process) ...	3200
Barley	3150
Oat meal	3150
Barley meal	3060
Wheat sharps	2910
Linseed meal (new process) ...	2890
Pea meal	2880
Oats	2750
Malt coombs	2640
Brewers' grains, dried ...	2540
Wheat bran	2450
Alsike clover hay	2170
Crimson clover hay ...	2110
Meadow fescue hay ...	2100
Lucerne hay	2100
Hay from mixed grasses ...	2080
Timothy hay	2050
Red clover hay	1880
Oat straw	1840
Rye straw	1820
Wheat straw	1630
Timothy grass	1040
Red clover, green	799
Potatoes	689
Whole milk	680
Brewers' grains, wet ...	674

Substance.	Fuel value of 1 gramme, in calories.
Lucerne, green	659
Crimson clover, green	511
Carrots	373
Swedes	365
Separated milk	362
Turnips	308
Mangolds*	285

Feeding Standards.—It will be remembered that food may be used by an animal in three ways:—

(1) To repair and renew its tissues.
(2) To furnish heat and energy (by oxidation).
(3) To promote growth and increase.

Since the requirements of an animal in these respects may vary greatly, it is obvious that the quantities of the chief constituents of food with which it should be provided will also vary. Many attempts to determine the amounts of the various food constituents required by various animals under different conditions have been made.

One of the earliest and still, perhaps, the most generally used series of standards was proposed by Wolff in 1864. The numbers suggested are what may be expected on the average to be suitable, but it is evident that much depends upon the individual animal and upon a number of other conditions difficult to specify.

WOLFF'S FEEDING STANDARDS.

Per day per 1000℔. live weight.

	Total organic matter. ℔.	Digestible food stuffs.			Approximate fuel value in ℔. of water raised 1° C.
		Protein. ℔.	Carbo-hydrates. ℔.	Fat. ℔.	
Ox, at rest	17·5	0·7	8·0	0·15	37,000
,, moderately worked	24·0	1·6	11·3	0 30	53,500
,, heavily worked	26·0	2·4	13·2	0·50	68,500
Horse, moderately worked	22·5	1·8	11·2	0·60	59,000

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* In England mangolds are usually of higher value than turnips or even swedes.

	Total organic matter. lb.	Digestible food stuffs.			Approximate fuel value in lb. of water raised 1° C.
		Protein. lb.	Carbo-hydrates. lb.	Fat. lb.	
Horse, heavily worked	25·5	2·8	13·4	0·80	74,000
Milch cow	24·0	2·5	12·5	0·40	65,000
Sheep, for wool, coarse	20·0	1·2	10·3	0·20	49,000
Ditto, fine	22·5	1·5	11·4	0·25	55,000
Fattening Cattle.					
First period	27·0	2·5	15·0	0·50	76,000
Second ,,	26·0	3·0	14·8	0·70	79,000
Third ,,	25·0	2·7	14·8	0·60	77,000
Fattening Sheep.					
First period	26·0	3·0	15·2	0·50	79,000
Second ,,	25·0	3·5	14·4	0·60	79,000
Fattening Pigs.					
First period	36·0	5·0	27·5		133,000
Second ,,	31·0	4·0	24·0		115,000
Third ,,	23·5	2·7	17·5		82,500

As already stated, the suitability of a particular ration depends upon many factors not easily measured. It is evident, therefore, that no standard ration can be arranged which will fit all cases. Individual peculiarity of the animal, local cheapness or dearness of particular classes of food stuffs, the value of the manure produced, and a number of other considerations must be taken into account in each case, especially when, as usually happens, the question is regarded mainly from a financial standpoint.

Another factor must not be lost sight of, especially in feeding young animals—the supply of a due proportion of mineral matter (phosphates, lime, &c.) for the formation of bone, &c. Fortunately ash is usually abundant in foods which are rich in albuminoids, so that in most cases the requirements of the animals for nitrogenous matter will enforce the use of foods containing also the requisite minerals. The importance of this point is shown by experiments on the feeding of pigs (i.) with maize meal only, (ii.) with pea meal and maize meal, equal weights, and (iii.) with one-third dried blood and two-thirds maize meal.* Lots (ii.) and (iii.) increased in weight more rapidly, their carcasses contained more blood and lean meat and less water, while their bones were much stronger and left more ash on burning than those of lot (i.).

In the case of dairy cows the ration certainly ought to vary with the milk-flow. This has been recognised in the standards proposed by Lehmann and by some American investigators.†

The table on the following page gives the standard rations for milch cows as suggested by these experimenters.

In this table no doubt the proper method of altering the rations would be in accordance with the amounts of solids yielded by the milk, *i.e.*, to consider not merely the quantity but also the composition of the milk yielded by the animals. With dairy cows, as a rule, the most vigorous eater is the most profitable animal.

Another point of some interest is the bulk of the food, especially for ruminating animals. American experiments have shown that while it is possible to successfully feed cows on concentrated foods (maize meal) only, for several months together, during which time chewing the cud entirely ceases, yet with calves, rumination is essential and death ensues if coarse forage be withheld,‡ even though abundance of milk and grain be supplied.

Quantity of Water consumed in proportion to Dry Food.—This varies considerably in different animals and with different conditions. According to Warington§ the normal amounts are—

For sheep ...	...	2 : 1
,, horses ...	...	2 to 3 : 1
,, cattle ...	...	4 : 1

With sheep, when fed on succulent food, no water to drink is as a rule required. In dry climates, however, a sheep will

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* Henry, Reports of Wisconsin Experiment Station 1886-89.

† Atwater and Phelps, Rep. of the Storrs Exp. Station 1897.

‡ *v.* Bulletins of the Utah (No. 46) and Illinois (21) Expt. Stations.

§ Chemistry of the Farm.

Milk per cow per day.	Dry matter. ℔.	Digestible nutrients.				Albuminoid ratio.
		Protein. ℔.	Fat. ℔.	Carbohydrates. ℔.	Fuel value. Calories, *i.e.*, kilos of water through 1° C.	
Lehmann's standard for cows of 1000℔. live weight.						
Yielding 11℔. of milk ...	25	1·6	0·3	10	22,850	1 : 6·7
,, 16½℔. ,, ...	27	2·0	0·4	11	25,850	1 : 6·0
,, 22℔. ,, ...	29	2·5	0·5	13	30,950	1 : 5·7
,, 27½℔. ,, ...	32	3·3	0·8	13	33,700	1 : 4·5
Atwater and Phelps's standard for cows of 950—1100℔. live weight.						
Yielding 10 to 20℔. milk ...	22—24	2·3	0·4—0·6	12—14	30,600	1 : 6·1
,, 20 ,, 25℔. ,, ...	23—25	2·6	0·5—0·7	12—14	31,600	1 : 5·5
,, 25 ,, 30℔. ,, ...	23—25	2·9	0·5—0·7	12—14	32,100	1 : 5·0
,, 30 ,, 35℔. ,, ...	24—26	3·2	0·6—0·8	13—15	34,900	1 : 4·9
,, 35 ,, 40℔. ,, ...	24—26	3·5	0·6—0·8	13—15	35,500	1 : 4·4

drink from 1 to 6 quarts of water per day. With roots, in winter, much more water than is necessary is taken, even though none be drunk, and the addition of a little dry food, meal or cake, is decidedly economical.

With horses the proportion of water consumed varies greatly with the amount of work done by the animal and with other circumstances.

With the Paris cab horses Grandeau found the average proportion of water to dry matter in the food to be 2 1 : 1 when at rest and 3·6 : 1 when working.

With fattening oxen, American experiments* showed that from 1·6 to 3·4℔. of water per ℔. of dry matter were consumed and that the largest amount of water was drunk when the food was richest in protein.

With milch cows the average amount of water to each pound of dry food is 4℔., according to American experiments; but here again a ration with a narrow albuminoid ratio requires more water than one with a wide one. Thus at the Wisconsin Station in 1886 it was found that with food having an albuminoid ratio of 1 : 5·5 there were 4·33℔. of water drunk for each pound of dry matter, while with a ratio of 1 : 8·6 only 2·41℔. were taken. A cow will usually drink from 8 to 10 gallons per day, but if roots be supplied the quantity will of course be considerably diminished.

With pigs the usual proportion of water consumed does not appear to have often been recorded. In 1887, at Copenhagen, trials showed no advantage or disadvantage between excessive quantities of water and an *ad libitum* supply. On the other hand, experiments conducted at the Yorkshire College Farm at Garforth in the early part of 1900 showed a decided advantage in curtailing the water supplied to fattening pigs. Two pens of six pigs each were fed with a mixture of equal weights of barley meal and "sharps." In one case the mixture was soaked for some days in four times its weight of water, while in the other only twice its weight of water was used. The former was fed to the pigs in a sloppy condition, the latter was of the consistency of oat-meal porridge. Both lots were allowed as much of the food as they would eat, and the animals receiving the drier food had access to a water trough. In eight weeks the pen getting the wetter food increased by 334lb., while the other gained 458lb. (live weights). The pigs of the former consumed 1904lb. of food, while those of the latter ate 2254lb. The proportions of food consumed to weight gained were—

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* Georgeson, Bull. 34 and 39, Kansas Expt. Station.

In those getting much water	...	5·7
In those getting little water	...	4·9

The pigs fed on the drier food thus made 124lb. more increase in live weight and yielded about 102lb. more pork, while each pound of increase in live weight was obtained by the expenditure of 0·8lb. of food less than with the other animals. The extra food cost about 19/-, but the value of the increased quantity of pork was about 42/6, leaving a net gain of 23/6 for the pen receiving the drier food.

Money Value of the Constituents of Food Stuffs.—Attempts have been made to fix money values to the albuminoids, carbohydrates, and fat present in food stuffs, so as to permit of the calculation of the value of a food from the results of its analysis, as has been done in the case of manures (*v.* Chap. VIII.).

The results of these attempts have not been entirely satisfactory, nor indeed can they be expected to be, since many of the most valuable properties of food stuffs, *e.g.*, flavour or palatibility, cannot satisfactorily be expressed quantitatively. Samples of food of desirable flavour and much relished by animals may often command a price much higher than could be deduced from their composition.

Wolff, long ago, deduced the ratios of the values of digestible carbohydrates, fats, and protein in many concentrated food stuffs at 1 : 3 : 2·4.

König gave 1 : 2·9 : 2·7, while in various States of America most discordant values were obtained, possibly owing to great local variations in prices,

In 1891, a long paper was read before the Surveyors' Institute on the subject by Kinch.* He points out that the physiological ratio of values of protein to carbohydrates would be about 6 : 1, since a ration having an albuminoid ratio of 1 : 6 is most generally suitable for feeding.

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* Abstract in J. Soc. Chem. Ind. 1892, 701.

By considering a large number of food stuffs and taking into account their relative consumption, he arrives at the ratio of 1 : 2·5 : 2·5 as the values of digestible carbohydrates, fats, and protein, the latter including both albuminoids and amides, the error introduced by including the latter as protein being counterbalanced by the fact that the manurial value of the undigested nitrogenous matter has been ignored.

He further estimates the value of digestible carbohydrates at 1·24 shilling "per unit" per ton, or say, practically, 1/3 "per unit" per ton.

The values of the three chief ingredients of feeding stuffs thus become—

	Per lb.	Per unit per ton.	
	d.	s	d.
Digestible carbohydrates ...	0·66	1	3
,, fat	1·66	3	1½
,, albuminoids and amides	1·66	3	1½

By adding the percentages of digestible fat and digestible protein together, multiplying their sum by 2·5, and adding the percentage of digestible carbohydrates, the number of "food units" in the food is obtained.

To calculate the value per ton, it is then only necessary to multiply the food units by 1/3.

It will be found, in practice, that if it be assumed that the *total* carbohydrates be worth 1/- per unit and the *total* fat and albuminoids 2/6 per unit, the value, calculated per ton on this basis, will be roughly correct.

It is obvious that accuracy is not possible in such calculations and that the values are liable to great fluctuations.

The Manurial Value of Foods.—When food is supplied to an adult animal which is not increasing in weight nor producing milk or wool, the whole of the manurial constituents of the food will be recovered in the excreta, and, if subsequent loss by fermentation or drainage be prevented, may be restored to the land.

It is otherwise with growing, fattening, or milking animals.

In such cases a portion, and sometimes a considerable portion, of the nitrogen, phosphoric acid, and potash is employed in forming the increase, and only the residue remains in the excreta for use as manure.

The proportion of the total nitrogen of the food retained by an animal varies greatly, not only with the individual, but also with the composition of the food.

A young calf fed on milk will retain as much as 69 or 70% of the nitrogen in its food, while a horse will, if full grown, excrete the whole.

According to Lawes and Gilbert,* the proportion of the total nitrogen of the food retained in the fattening increase of oxen and sheep varies from about 3% with decorticated cotton cake (containing 6·6% of total nitrogen) to as high as 14% with oat straw (containing only 0·5% of total nitrogen). With many foods it averages about 5 or 6% of the total nitrogen in the food. With phosphoric acid the same investigators found that from 3 or 4% (with bran, malt coombs, &c.) to 19 or 20% (with maize, rice meal, barley straw, oat straw, &c.) of the total present in the food was retained by fattening oxen and sheep. With potash the corresponding figures were 0·3 or 0·4% (with roots) to 3 or 4% (with malt, maize, &c.).

The Rothamsted experiments, as summarised by Warington†, yielded the following results:—

	Percentage of nitrogen obtained as increase or voided in manure.		
	% in carcass or milk.	% in urine.	% in total excrements.
Horse working ...	0·0	70·6	100·0
Fattening ox ...	3·9	73·5	96·1
,, sheep ...	4·3	79·0	95·7
,, pig ...	14·7	60·3	85·3
Milch cow ...	24·5	57·4	75·5
Calf fed on milk ...	69·3	25·6	30·7

With the ash constituents the following were the results:—

	For 100 consumed as food.	
	In live-weight increase or milk.	Voided as manure or in perspiration.
Horse ...	0·0	100·0
Fattening ox ...	2·3	97·7

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* J.R.A.S. 1885, 600.

† Chemistry of the Farm, 162.

	For 100 consumed as food.	
	In live-weight increase or milk.	Voided as manure. or in perspiration.
Fattening sheep	3·8	96·2
,, pig ...	4·0	96·0
Milch cow ...	10·3	89·7
Calf fed on milk	54·3	45·7

Lawes and Gilbert* give the average manurial value per ton of the common feeding stuffs as deduced from experiments, assuming that they are supplied to fattening sheep and oxen. The figures are based on the assumption that ammonia is worth about 6d., potash about 2½d., and phosphoric acid about 3d. per pound.

The table on p. 304 is abridged and altered to suit present prices from the large table given by them, and will suffice to show the plan adopted in calculating the values.†

Lawes and Gilbert in the same paper also give their estimate of the unexhausted manurial value of foods used on a farm in previous years.

They conclude that with all foods, excepting hay and straw, the compensation value of food used the previous year is one-half the original manurial value and that the value diminishes each year by one-third of its value the previous year. In the case of hay and straw they state that two-thirds of its original manure value should be deducted for the first year and afterwards one-third from year to year.

Consider, for example, the case where linseed cake had been used for several years on a farm. The following shows the compensation value of the unexhausted manure for six years, assuming that the same food has been supplied yearly:—

1 ton linseed cake.

Original value.			Last year. (1st year back)			2nd year back			3rd year back.		4th year back.	
£	s.	d.	£	s.	d.	£	s.	d.	s.	d.	s.	d.
3	6	5	1	13	2	1	2	1	14	9	10	2

5th year back.		6th year back.		Total.		
s.	d.	s.	d.	£	s.	d.
5	9	3	10	4	9	9

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[*] J.R.A.S. 1885, 600.

[†] The value of nitrogen has been taken at 6d., of potash 2d., and of phosphoric acid 3d. per lb.

	Food required for 1lb. increase.	Nitrogen.						Phosphoric acid.					Potash.					Value of manure from 1 ton of food.		
		In 1 ton of food.	In increase from 1 ton of food.	In manure.	Value at 6d. per lb.			In 1 ton of food.	In increase from 1 ton of food.	In manure.	Value at 3d. per lb.		In 1 ton of food.	In increase from 1 ton of food.	In manure.	Value at 2d. per lb.				
		lb.	lb.	lb.	£	s.	d.	lb.	lb.	lb.	s.	d.	lb.	lb.	lb.	s.	d.	£	s.	d.
Linseed cake	6·0	106·40	4·74	101·66	2	10	10	44·80	3·21	41·59	10	5	31·36	0·41	30·95	5	2	3	6	5
D. cotton cake	6·5	147·84	4·38	143·46	3	11	9	69·44	2·96	66·48	16	7	44·80	0·38	44·42	7	5	4	15	9
U. cotton cake	8·0	84·00	3·56	80·44	2	0	3	44·89	2·41	42·39	10	7	44·80	0·31	44·49	7	5	2	18	3
Beans ...	7·0	89·60	4·06	85·54	2	2	9	24·64	2·75	21·89	5	6	29·12	0·35	28·77	4	9	2	13	0
Maize ...	7·2	38·08	3·95	34·13	0	17	0	13·44	2·68	10·76	2	8	8·29	0·34	7·95	1	4	1	1	0
Wheat ...	7·2	40·32	3·95	36·37	0	18	2	19·04	2·68	16·36	4	1	11·87	0·34	11·53	1	11	1	4	2
Barley ...	7·2	36·96	3·95	33·01	0	16	6	16·80	2·68	14·12	3	6	12·32	0·34	11·98	2	0	1	2	0
Oats ...	7·5	44·80	3·79	41·01	1	0	6	13·44	2·57	10·87	2	8	11·20	0·33	10·87	1	10	1	5	0
Bran ...	9·0	56·00	3·16	52·84	1	6	5	80·64	2·65	78·50	19	8	32·48	0·27	32·21	5	4	2	1	5
Clover hay ...	14·0	53·76	2·03	51·73	1	5	10	12·77	1·38	11·39	2	10	33·60	0·18	33·42	5	7	1	14	3
Meadow hay ...	15·0	33·60	1·90	31·70	0	15	10	8·96	1·28	7·68	1	11	35·84	0·16	35·68	5	11	1	3	8
Barley straw ...	23·0	8·96	1·24	7·72	0	3	10	4·03	0·84	3·19	0	9	22·40	0·11	22·29	3	9	0	8	4
Swedes ...	109·1	5·60	0·26	4·64	0	2	4	1·34	0·18	1·16	0	4	4·93	0·02	4·91	0	10	0	3	6
Mangolds ...	96·0	4·93	0·30	4·63	0	2	4	1·57	0·20	1·37	0	4	8·96	0·03	8·93	1	6	0	4	2

CHAPTER XIV.

MILK AND MILK PRODUCTS.

MILK is the natural secretion of the special glands of a female, intended for the nourishment of the new-born. The mammary glands are, in general, only developed in the female and are active in producing their secretion for a certain period after parturition. In certain abnormal instances, however, males have been known to produce milk; but such cases are rare.

The milks of different animals differ considerably both in the constituents present and in the proportions of the constituents.

The milk of the cow is the most important and has been studied in greatest detail.

The constituents of milk are usually divided into—

Water,
Fat,
Albuminoids,
Sugar,
Ash.

A short account of the chemical nature of these constituents (excluding water) may be here given.

Fat.—The fat present in milk resembles in general constitution the true animal and vegetable fats already described (see p. 202). Like them it consists of a mixture or compound of the glyceryl salts of fatty acids.

It differs, however, from other oily substances in the character of the fatty acids present.

In milk fat considerable quantities of acid radicals of low molecular weight are present, besides the stearic, oleic, and other heavy acids found in other fats.

In common with most natural fats it is probably a mixture, though whether each acid radical is present as a distinct glyceryl salt or whether two or three different acid radicals may be attached to the same glyceryl group is uncertain. The latter hypothesis is probably more correct.

The proportions of the various fatty acids found in butter are subject to considerable variation according to the food; they are said also to vary with the season of the year. The fat of milk given by cows soon after calving is said to be much richer in volatile fatty acids than that of cows in the later stages of lactation.

Assuming that the glyceryl salts are present as separate individuals (which, as already stated, is probably not the case), the chief constituents of butter fat are given by Richmond* as follows :—

		%
Glyceryl tributyrate, $C_3H_5(C_4H_7O_2)_3$	about	3·85
,, tricaproate, $C_3H_5(C_6H_{11}O_2)_3$	,,	3·60
,, tricaprylate, $C_3H_5(C_8H_{15}O_2)_3$	,,	0·55
,, tricaprate, $C_3H_5(C_{10}H_{19}O_2)_3$	,,	1·90
,, trilaurate, $C_3H_5(C_{12}H_{23}O_2)_3$	,,	7·40
,, trimyristate, $C_3H_5(C_{14}H_{27}O_2)_3$	,,	20·20
,, tripalmitate, $C_3H_5(C_{16}H_{31}O_2)_3$	,,	25·70
,, tristearate, $C_3H_5(C_{18}H_{35}O_2)_3$	,,	1·80
,, trioleate, $C_3H_5(C_{18}H_{33}O_2)_3$, &c.	,,	35·00
		100·00

According to the recent analyses of C. A. Browne† the fatty acids derived from 100 grammes of butter consisted of—

	Grammes.
Dihydroxystearic acid, $HC_{18}H_{33}(OH)_2O_2$...	1·00
Oleic acid, $HC_{18}H_{33}O_2$	32·50
Stearic acid, $HC_{18}H_{35}O_2$	1·83
Palmitic acid, $HC_{16}H_{33}O_2$	38·61
Myristic acid, $HC_{14}H_{27}O_2$	9·89
Lauric acid, $HC_{12}H_{23}O_2$	2·57
Capric acid, $HC_{10}H_{19}O_2$	0·32
Caprylic acid, $HC_8H_{15}O_2$	0·49
Caproic acid, $HC_6H_{11}O_2$	2·09
Butyric acid, $HC_4H_7O_2$	5·45
	94·75

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* Dairy Chemistry, p. 35.

† Jour. Chem. Soc. 1900, abst. ii. 55.

The following table gives the results of analyses of butter fat and of "margarine" and suet[*]:—

	Good butter.	Poor butter.	Margarine.	Suet.
Butyric acid ...	5·3 to 6·1	4·6 to 5·1	0·5	0·27
Caproic acid ...	3·2 to 3·7	2·8 to 3·1	0·3	0·17
Total volatile acids ...	8·6 to 9·7	7·2 to 8·8	0·8	0·44
Solid non-volatile acids	82·3 to 82·9	83·8 to 84·6	93·4	91·12

Blyth and Robertson[†] have separated butter into a solid crystalline fat and an oil in the proportions of about 45·5 of butter oil to 54·5 of butter crystals. They ascribe the formula $C_3H_5\begin{cases}C_4H_7O_2\\ C_{16}H_{31}O_2\\ C_{18}H_{34}O_2\text{‡}\end{cases}$ to the solid crystalline body and conclude that butter is mainly made up of compound and not of simple triglycerides.

All the acids, with the exception of the oleic acid, are saturated compounds of the general formula $C_nH_{2n+1}.COOH$. Acids of low molecular weight are liquids soluble in water and volatile in steam; such are butyric acid, C_3H_7COOH, caproic acid, $C_5H_{11}COOH$, and caprylic acid, C_7H_5COOH, whilst capric and lauric acids are very slightly soluble and volatile.

The acids of higher molecular weight are solid, insoluble in water, and non-volatile.

Milk fat, in addition to the above, contains traces of cholesterol, $C_{26}H_{43}OH$, lecithin, $C_3H_5.(C_{18}H_{85}O_2)_2.[HPO_4.N(CH_3)_3C_2H_4(OH)]$ (not more than ·5% of the fat), and a colouring substance of unknown composition, which has been called "*lacto-chrome.*" Milk fat is a variable mixture of chemical compounds and therefore liable to considerable variation in properties. Moreover its physical constants, *e.g.*, melting point, are not sharply defined. It is insoluble in water, though capable of dissolving about $\frac{1}{500}$ of its weight of water. It is non-volatile at 100°, but in contact with air absorbs oxygen and thus increases in weight; this, no doubt, is because of the unsaturated fatty acids (oleic acid, &c.) present. It melts between 29·5° and 33° C. (Richmond) and is therefore liquid in the animal. Its specific gravity varies, but is usually ·930 at 15°, compared with water at the same temperature, at $\frac{37·8°}{37·8°}$ (liquid) = ·9118, at $\frac{39·5°}{39·5°}$ = ·9113.

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[*] Viollette, J.C.S. 1891, abst. 869. [†] Proc. Chem. Soc. 1889, 5.

[‡] So given in the "Proceedings"; probably oleic acid radical, $C_{18}H_{33}O_2$, is meant.

Solid fat is heavier, volume for volume, than the liquid form at the same temperature (Richmond); so that evidently contraction occurs at the moment of solidification. By very slow cooling of melted butter fat a partial separation of the various glyceryl salts occurs, the portion solidifying first being characterised by containing less volatile acids and less oleic acid or other unsaturated acids than the portion remaining liquid.

The index of refraction of milk fat varies from 1·4550 to 1·4586 at 35°; the heat of combustion of 1 gramme is 9231·3 calories.* It is soluble in hydrocarbons, in ether, carbon disulphide, acetone, nitrobenzene, and in warm amyl alcohol.

The composition of butter fat is liable to considerable variation, being affected by the food, period of lactation, and other conditions affecting the cows. It has been observed that large quantities of cotton cake have a marked effect upon the butter and cause it to become harder and whiter, and to give the reactions for cotton-seed oil. This effect has been noticed within 24 hours after feeding with cotton cake commenced.† Sesame-oil cake, almond cake, and cocoanut-oil cake used as food for cows alter the iodine value and percentage of volatile fatty acids of the butter fat.‡ Reference to the change in composition of butter fat with advancing lactation has already been made.

The fat exists in the milk as minute globules of diameters varying from ·0016 to ·010mm. The number of globules in milk is astonishingly great, being estimated by different observers at from 1·52 to 11·4 millions in the cubic millimetre. The globules vary greatly in size in any particular sample, but certain breeds of cows are remarkable for the preponderance of large-sized or of small-sized globules. It has been suggested that the fat globules are surrounded by an albuminous membrane, but this theory does not receive much support at present, and the generally accepted view is that the fat is in the form of a true emulsion, each globule being surrounded by a layer of liquid, held in position by surface attraction.

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* Stohman & Langbein, Jour. Chem. Soc. 1891, abst. 11.

† Thorpe, J.C.S. 1900, abst. ii. 237.

‡ Baumert and Falke, Zeitschrift Untersuch. d. Nährungs- & Genussm. 1898, 665.

Rancidity.—When butter fat becomes rancid the chief changes are probably the hydrolysis of a portion of the fat into free acids and glycerol, *e.g.*, $C_3H_5(C_4H_7O_2)_3 + 3H_2O = C_3H_5(OH)_3 + 3HC_4H_7O_2$. The glycerol probably oxidises to acroleïn, C_3H_4O, or acrylic acid, $C_3H_4O_2$. The fatty acids remain free, and those which are volatile, *e.g.*, butyric acid, give rise to the odour of rancid butter. Oleic acid and other unsaturated acids are oxidised, yielding substances some of which are soluble in water, and which cause butter which has become rancid to give a brown colouration when dissolved in warm alkali.

Albuminoids.—Much work has been done in connection with the detection and separation of the proteids present in milk, and very different views as to their number and nature are held by various investigators.

Duclaux affirms that casein is the only proteid present, but that it exists in three forms—*casein in suspension, colloidal casein*, and *casein in solution*. The latter is found in the filtrate when milk is passed through a porous earthenware cell, while the other two are retained. The amount of the soluble casein is about one-eighth of the total proteid. The colloidal casein is that found in whey after the rennet has precipitated the suspended casein. He quotes the following numbers[*] as the results of an examination of milk and the whey formed from it:—

	In suspension.		In solution.	
	Milk.	Whey.	Milk.	Whey.
Fat	4·30	0·85	—	—
Sugar	—	—	5·37	5·73
Casein	3 53	0·46	0·37	0·36
Calcium phosphate...	0·23	—	0·17	0·17
Salts	—	—	0·40	0·43
	8·06	1·31	6·31	6·69

Hammarsten (1872—1877) describes two albuminoids—

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[*] Compt. Rend. 98, 438; Jour. Chem. Soc., abst. 1884, 762.

casein and *albumin;* Halliburton[*] also gives two—*caseinogen* and *albumin.*

Engling and Sebelien[†] in addition found *globulin.* Danilewsky and Radenhausen (1880) described at least five proteids as present in milk. The presence of casein or caseinogen, albumin, and globulin is generally admitted, while one or two others are possibly present in very small proportion.

Casein or, according to modern nomenclature, *caseinogen,* is a white amorphous body, devoid of taste or smell, insoluble in water, alcohol, or ether, soluble in dilute alkalies or solutions of alkaline carbonates or phosphates. It is insoluble in dilute but dissolves in strong acids.

It is capable of uniting with calcium salts, particularly the phosphate, with which it is associated in milk and from which it is freed with difficulty.

According to Halliburton's nomenclature, casein is the name given to the curd formed by the action of rennet upon milk. In the milk *caseinogen* exists and can be precipitated by acids.

Various analyses of casein have been published. The following by Chittenden and Painter may be taken as typical:—

			%
Carbon	...	...	53·30
Hydrogen	...	...	7·07
Oxygen	...	...	22·03
Nitrogen	...	...	15·91
Phosphorus	...	...	0·87
Sulphur	...	...	0·82

Caseinogen is capable of coagulation in two ways—by the action of an acid, less acid being required at high than at low temperatures; or by the action of the enzyme contained in rennet known as rennin, lab, chymosin, or pixine. This ferment is found in the stomachs of a large number of animals, being generally more abundant in young than in adult individuals. It or a ferment possessed of similar powers is found in birds, fishes, and in many plants; also as a product of the action of certain bacteria. In the case of acid coagulation the curd formed consists of the unaltered caseinogen and is almost free from calcium compounds.

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[*] Chemical Physiology.

[†] Jour. Soc. Chem. Ind. 1886, 387.

With rennet the effect is very different; the caseinogen is changed into two proteids, one of which only is readily coagulated, the other with difficulty. The former is at once coagulated by the calcium salts (mainly phosphate) present in cows' milk, and forms, with the entangled fat, the curd; the latter goes into the whey and can be coagulated by heating to 95° or 100°. The curdling of milk by rennet is thus dependent upon the presence of calcium phosphate in the milk. Hammarsten has proved that in the absence of calcium phosphate or other salts of the alkaline earths rennet will not curdle milk.

Under ordinary circumstances rennet acts best at about 35° and is killed or destroyed at 70°.

The *albumin* of milk closely resembles serum albumen of blood. It is in complete solution in milk but is coagulated at 72°, or by saturation with sodium sulphate at 30°, or ammonium sulphate at ordinary temperatures, but not by magnesium sulphate at 40°. It is also precipitated by copper, mercury, or lead salts, by tannin, and by alcohol.

Its composition, according to Sebelien,* is—

			%
Carbon	...	...	52·19
Hydrogen	...	...	7·18
Oxygen	...	...	22·90 to 23·13
Nitrogen	...	...	15·77
Sulphur	...	...	1·73 to 1·96

It differs in composition from casein in containing no phosphorus, more carbon, and more than twice as much sulphur.

Many other proteids have been described as occurring in cows' milk, but some doubt as to whether they are not formed by the action of the reagents employed upon the casein or albumen has been expressed. As an illustration of the complexity of the method adopted for the separation and preparation of some of the proteids, the following account of two proteids recently analysed and described by Storch may be given.† Skimmed milk was mixed with three times its volume of saturated solution of sodium sulphate and a few drops of egg albumen and heated to 100°. The coagulated casein was filtered off, and to the filtrate more sodium sulphate solution, a trace of acetic acid, and solid sodium sulphate in excess were added, when a substance, A, was precipitated; to the filtrate strong acetic acid was added, when another precipitate, B, was formed, and the liquid was then found to be free from proteids.

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* Jour. Soc. Chem. Ind. 1886, 387.

† Jour. Chem. Soc., abst. ii. 1897, 420; 1900, abst. i. 266.

Substance A (the yield of which was about 2% of the milk) was found to contain calcium and to be soluble in water, from which acetic acid reprecipitates it free from calcium and insoluble in water, though soluble in alkalies. Substance B was free from calcium and insoluble in water; its amount corresponded to about 0·3% of the milk. A was coagulated by rennet, B was not. On analysis of the purified substances the following figures were obtained:—

	A.	B.	Casein (Hammarsten). %
Carbon ...	54·43	49·13	53·00
Hydrogen ...	6·81	5·91	7·00
Oxygen ...	22·52	27·14	22·65
Nitrogen ...	14·82	14·13	15·70
Sulphur ...	0·63	1·58	0·80
Phosphorus ...	0·79	2·09	0·85

A globulin (Engling) and a fibrin (Babcock) have also been described as occurring in small quantities in milk. For all ordinary purposes, however, the proteids of milk may be considered as being composed mainly of casein or caseinogen and lact-albumin, the amount of the latter being usually about one-seventh of that of the former.

According to recent researches* milk contains a substance—carnic acid, $C_{10}H_{15}N_3O_5$—in union with phosphoric acid, the amount in cows' milk being 0·056%, in human milk 0·124%, of *phosphorcarnic acid* or *nucleon.* The compound phosphorcarnic acid is said also to occur in plants, especially during germination and blossoming.

Milk Sugar—*Lactose* or *Lacto-biose*—occurs in the milk of animals in varying quantities. It has not, with certainty, been detected in plants.

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[*] Wittmaack and Siegfried, Jour. Chem. Soc. 1897, abst. ii. 220, and Stocklasa, ditto, 573.

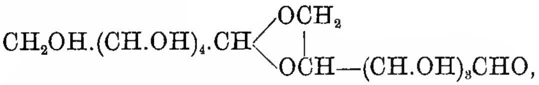
Five different modifications of milk sugar have been described—one hydrated crystalline form, $C_{12}H_{22}O_{11}+H_2O$, three anhydrous crystalline, and one anhydrous amorphous form.

The hydrated substance is the most important. It forms large transparent rhombic or monoclinic crystals, which possess well-marked cleavage. Its specific gravity is 1·534. It possesses a faint sweet taste. The crystals are stable at 100°, but at about 130° they begin to lose water, and decompose at 180° with partial charring.

Milk sugar dissolves in 5·87 parts of water at 10° or in 2·5 parts at 100°. The solution saturated at 10° contains 14·5 % of sugar and has a specific gravity of 1·055. By spontaneous evaporation the solution becomes supersaturated and does not deposit crystals until it contains over 21 % of sugar. By cooling hot saturated solutions down to ordinary temperatures in closed vessels no crystallization occurs and a highly supersaturated solution is obtained. The crystals are insoluble in alcohol or ether, but very soluble in hot acetic acid.

Lactose resembles glucose in possessing reducing properties, as shown by its action upon ammoniacal silver solution in the cold and upon alkaline copper solutions on heating. This is in consequence of its containing an aldehyde group, and on hydrolysis either by dilute acids or by an enzyme known as *lactase* it yields glucose and galactose.

According to E. Fischer[*] the constitution of milk sugar is expressed by the formula—



$$CH_2OH.(CH.OH)_4.CH\left\langle\begin{array}{l}OCH_2\\ \;| \\ OCH—(CH.OH)_3CHO,\end{array}\right.$$

so that on hydrolysis there results—

$$CH_2OH(CH.OH)_4CHO \text{ and } CH_2OH(CH.OH)_4.CHO,$$

i.e., the two isomeric aldoses—glucose and galactose.

Milk sugar does not readily undergo alcoholic fermentation, but by the action of certain yeasts, aided perhaps by the hydrolysing enzyme lactase, it can be induced.

It is much more prone to undergo the lactic fermentation. This is brought about by micro-organisms, which are always abundant in dairies, &c., though probably all are not of the same kind. The chemical change involved is apparently of a very simple character—

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[*] Ber. 21, 2631; Jour. Chem. Soc. 1888, abst. 1267.

$$C_{12}H_{22}O_{11}+H_2O = 4C_2H_4(OH)COOH,$$

but in many cases other products are formed and much more complicated reactions must occur.

Milk sugar is prepared from whey or from milk by removing the nitrogenous matter and fat by means of mercuric nitrate, precipitating the mercury from the filtrate by addition of caustic soda and sulphuretted hydrogen, and evaporating the clear liquid until the milk sugar crystallizes out on cooling.

The reaction of milk towards indicators depends, of course, greatly upon the indicator.

Fresh milk is usually described as *amphoteric* when tested with delicate litmus paper, *i.e.*, it turns red litmus blue and blue litmus red. Towards phenol-phthalein milk is distinctly acid. It should always be borne in mind that the nature of the reaction of a product containing organic acids and acid phosphates, as milk does, depends mainly upon the character of the indicator used. On keeping, milk almost invariably becomes more and more acid owing to the activity of the lactic bacilli, the development of acidity being more rapid in warm than in cold weather. The average acidity of milk as sold probably corresponds to about 0·2% lactic acid. As the acidity increases a sour taste becomes perceptible (at about 0·40%) and when the amount reaches 0·7% coagulation or curdling is produced. However long it may be kept, milk rarely develops an acidity exceeding 2% lactic acid.

The Ash of Milk is white and contains the inorganic constituents, together with some products resulting from the oxidation of the sulphur, phosphorus, and carbon existing in the proteids and other organic compounds. In the milk the ash constituents doubtless exist in very different states of combination to those in which they are left in the ash. The amount of ash in milk is usually about 0·7% and its composition varies slightly.

Schrodt and Hansen* give the following numbers as the extremes of seven analyses of the mixed milk of 10 cows taken at various times of the year :—

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* Jour. Chem. Soc. 1884, abst. 1397.

	%		%
Potash	22·55	to	26·94
Soda	10·26	to	11·97
Lime	19·71	to	23·57
Magnesia	1·78	to	3·15
Ferric oxide	traces	to	0·21
Sulphur trioxide	3·75	to	4·38
Phosphorus pentoxide	22·41	to	26·51
Chlorine	13·15	to	16·15

Of the ash about one-third is usually soluble in water and consists mainly of alkaline chlorides and carbonates. Much of the basic material of the ash exists in the milk in association with the casein and in union with citric acid.

Citric acid is present in milk to the extent of about 0·1 %[*] and crystals of calcium citrate are sometimes found in condensed milk. The presence of the citric acid probably accounts for a portion of the calcium phosphate of milk being in solution.

The gases contained in milk are chiefly carbon dioxide, oxygen, and nitrogen. From a litre of milk Pflüger (1869) obtained 1 c.c. oxygen, 76 c.c. carbon dioxide, 7 c.c. nitrogen.

Cows' Milk.—Cows' milk, being the most important from a commercial and agricultural standpoint, has been studied much more thoroughly than the milk of other animals.

Cows' milk is a white, or yellowish white, opaque liquid of sweet taste. Its specific gravity varies usually between 1·027 and 1·034, but in certain cases may be outside these limits.

When freshly drawn and quickly cooled, milk has a certain specific gravity, but shows a decided increase in density (about ·0005) on keeping at the same temperature for some hours. This phenomenon, known as Recknagel's phenomenon,[†] has been attributed to a molecular change in the casein and to the presence of air bubbles, which gradually escape ; but is more likely to be due, as suggested by Richmond, to the fact that the fat globules, liquid at the temperature of the cow, do not at once solidify on cooling, but remain for some time in a super-cooled liquid condition. Since contraction occurs when milk fat solidifies, their slow solidification during standing would cause an increase in density.

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[*] Henkel & Soxhlet, Jour Chem. Soc. 1889, abst. 178.

[†] Berichte 14, 2684

The maximum density of milk is, unlike that of water, coincident with its freezing point, about −0·55° C. or −0·3° C. (Fleischmann). It expands when heated at a rate which naturally is dependent upon its composition, but is usually about ·0002 for each degree Centigrade.

According to Fleischmann* the coefficient of expansion of milk increases with the temperature and with the proportion of solid matter present. He found that the variations in volume of ordinary milk (of specific gravity 1·0315 at 15°) were as follows :—

	1,000,000	volumes at	0° C.
become	1,000,030	,,	1° C.
	1,000,391	,,	4° C.
	1,001,273	,,	10° C.
	1,002,134	,,	15° C.
	1,003,800	,,	20° C.
	1,006,414	,,	30° C.
	1,014,277	,,	50° C.
	1,019,243	,,	60° C.

When milk is heated the albuminoids apparently suffer decomposition and sulphuretted hydrogen is evolved.

The specific heat of milk is about 0·847. Its refractive index (*i.e.*, of the milk serum) is usually about 1·35. Skimmed milk and whey show very similar numbers.

Chemical Composition.—Cows' milk varies considerably in composition, its quality being dependent upon many circumstances, *e.g.*, food, health, breed, age, &c., &c., of the animals.

The *mean* composition is given by Richmond† as—

	%
Water	87·10
Fat	3·90

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[*] The Book of the Dairy, 1896, 13.

[†] Dairy Chemistry, 120.

	%
Milk sugar	4·75
Casein	3·00
Albumen	0·40
Ash	0·75

Colostrum.—The first milk after calving is known as colostrum, or "beestings," and is essentially differerent from normal milk.

It is a yellow liquid, with strong pungent taste, containing large numbers of small clusters of cells—"colostrum granules"—which vary in diameter from ·005 to ·025mm. and apparently result from the breaking up of the milk glands.

Engling* gives the composition of the colostrum of 22 cows as varying between—

Fat	1·88 to 4·68
Casein	2·64 to 7·14
Albumin	11·18 to 20·21
Sugar	1·34 to 3·83
Ash	1·18 to 2·31
Total solids ...	24·34 to 32·57
Specific gravity ...	1·059 to 1·079

The fat of colostrum has a higher melting point (40°—46°) and contains less of the volatile fatty acids than ordinary milk fat. The sugar present is largely grape sugar. Urea has been found in colostrum. The ash differs from that in normal milk in the smaller amount of potash and the much larger quantity of phosphorus pentoxide (up to 41·4%). The liquid secreted by a cow gradually changes day by day until in four or five days it approaches normal milk in composition, though the "colostrum granules" can be detected in the milk for 14 days or more after calving.

Influence of breed.—Great variations, especially in the proportion of fat, are shown by the milks of different races. The following numbers were obtained at the New York Experiment Station in 1891†:—

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* Jour. Chem. Soc. 1879, abst. 815; also Ladenburg's Handwörterbuch der Chemie.

† v. Report of Director, p 141.

Average composition of milk.

Breeds.	No. of analyses.	Water.	Fat.	Sugar.	Casein.	Ash.	Total solids.
Jersey ...	238	84·60	5·61	5·15	3·91	0·743	15·40
Guernsey ...	112	85·39	5·12	5·11	3·61	0·753	14·60
Devon ...	72	86·26	4·15	5·07	3·76	0·760	13·77
Ayrshire ...	252	86·95	3·57	5·33	3·43	0·698	13·06
American Holderness ...	124	87·37	3·55	5·01	3·39	0·698	12·63
Holstein Friesian ...	132	87·61	3·46	4·84	3·39	0·735	12·39

Vieth[*] gives the following averages :—

Breeds.	Fat.	Total solids.	Solids not fat.
Dairy shorthorn ...	4·03	12·90	8·87
Pedigree ,, ...	4·03	12·86	8·83
Jersey	5·66	14·89	9·23
Kerry	4·72	13·70	8·98
Red polled	4·34	13·22	8·88
Sussex	4·87	14·18	9·31
Montgomery ...	3·59	12·61	9·02
Welsh	4·91	14·15	9·24

Another important point in which the milks of cows of different breeds differ is in the average size of the fat globules. In any one sample of milk the globules are very varied in size, but their average dimensions can be estimated. At the New York Experiment Station in 1891 a large number of measurements of the size of globules of fat in the milk of cows of various breeds was made; the results are briefly summarised in the following table :—

Average diameter of milk globules from cows of various breeds during whole period of lactation.

Breed.	Diameter in fractions of an inch.	Ratio.	Diameter in millimetres.
Guernsey	$\frac{1}{9344}$	1·33	0·00270
Jersey	$\frac{1}{9631}$	1·30	0·00265
Devon	$\frac{1}{10370}$	1·20	0·00245
American Holderness ...	$\frac{1}{11274}$	1·10	0·00225
Holstein Friesian ...	$\frac{1}{12090}$	1·04	0·00210
Ayrshire	$\frac{1}{12446}$	1·00	0·00205

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[*] Quoted by Richmond, Dairy Chemistry, p. 125.

In all cases globules much larger (and also smaller) than the dimensions given occur, but in Guernsey and Jersey cows the larger globules constitute the greater portion of the total fat in the milk, while in Ayrshire cows the large globules are very few and constitute only a small proportion of the total fat present.

These facts have an important influence on the readiness with which the removal of cream can be effected, for it is obvious that large globules possess greater buoyancy and therefore rise to the surface much more rapidly than the small ones. In fact the very small ones probably never separate at all.

Morning's milk is said to have larger globules than evening's milk.* Change from dry winter food to green food in spring increases the size of the globules.†

Influence of period of lactation.—As a general rule it seems that the proportion of solids in milk diminishes for a short time after calving, then begins to increase and continues to do so to the eighth or ninth month after calving. The following figures are from the experiments at New York Experiment Station already alluded to and give the average results obtained with 14 cows:—

Composition of milk during each month of lactation.

Period of lactation.	Fat.	Casein.	Sugar.	Ash.	Total solids.
First month ...	4·86	3·53	5·00	0·69	14·09
Second ,, ...	4·13	3·05	5·20	0·72	13·13
Third ,, ...	4·03	3·23	5·01	0·71	13·04
Fourth ,, ...	4·22	3·42	5·06	0·70	13·36
Fifth ,, ...	4·23	3·32	5·29	0·70	13·56
Sixth ,, ...	4·35	3·61	5·24	0·73	13·90
Seventh ,, ...	4·39	3·51	5·42	0·74	14·08
Eighth ,, ...	4·39	3·51	5·35	0·74	14·00
Ninth ,, ...	4·51	3·80	5·13	0·71	14·17
Tenth ,, ...	4·46	3·81	5·39	0·73	14·41

The American observers also note a marked diminution in the average size, but a great increase in the number of fat globules with the advance of lactation.

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* Woll, Agric. Science 1892, 441.

† Schnellenberger, Milch Zeitung 1893, 817.

The author's experience agrees with the results of the American investigation. The results of about 700 analyses of the milk of 17 cows made in the spring of 1900, classified according to the month of lactation of the cows when the milk was collected, gives the following table:—

Period of lactation	Fat.	Solids not fat.	Total solids.
First month	4·11	8·91	13·02
Second ,, ...	3·40	8·81	12·21
Third ,, ...	3·65	8·99	12·64
Fourth ,, ...	—	—	—
Fifth ,, ...	3·70	9·00	12·70
Sixth ,, ...	3·82	9·08	12·90
Seventh ,, ...	—	—	—
Eighth ,, ...	4·30	9·31	13·61
Ninth ,, ...	4·35	9·37	13·72
Tenth ,, ...	—	—	—
Eleventh ,, (evening only)	5·48	9·65	15·13

Influence of food.—The character of the food of a cow has an influence on the quantity and quality of the milk only between narrow limits unless incipient starvation be induced. Rich, palatable, concentrated food is conducive to an increase both in the quality and quantity of the milk, but only up to a certain point. It is usually asserted that the use of succulent or sloppy food to stall-fed cows increases the quantity but reduces the quality of the milk; but according to Danish and American experiments this is not quite true. At Copenhagen (20th Report, 1890), for example, experiments conducted with 636 cows for three years showed that the addition of 40℔. of mangels or 50℔. of turnips per day increased the daily milk yield by over ·2℔., while the animals increased in weight and consumed 3·08℔. less straw daily; but no appreciable alteration in the composition of the milk could be detected.

Many investigations as to the influence of food upon milk production have been made in America.* The majority of these have been directed to contrasting the effects of rations with wide and with narrow albuminoid ratios, and the results show that a distinct improvement both in the quality and quantity of the milk can clearly be detected when the food of the cows is changed to a more nitrogenous ration. Thus in tests including some 150 animals the following mean results were obtained :—

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* *v* Reports of the Storrs Agric. Expt. Station 1894-97.

		Wide ratio.	Narrow ratio.
Average weight of cow		765℔.	765℔.
Daily rations per head	Digestible protein	1·78℔.	2·40℔.
	Fuel value of nutrients	28,100	26,600
	Albuminoid ratio	1 : 7·7	1 : 5·1
	Total cost	18·1 cents	17·2 cents
	Net cost*	9·9 ,,	8·1 ,,
Average daily yield	of milk	18·0℔.	18·2℔.
	of butter†	1·00℔.	1·04℔.
Cost of food	to produce 100℔. of milk, total	103 cents	97 cents
	,, ,, ,, net*	56 ,,	45 ,,
	to produce 1℔. of butter, total	19 ,,	17 ,,
	,, ,, ,, net*	10 ,,	8 ,,

It is very doubtful whether these changes, clear and distinct though they are, are of more than a temporary character.

The improvement in the amount and quality of milk which usually ensues when cows are turned out to pasture in the early spring is not to be attributed entirely to the change of food, but largely to the more healthy and natural character of the conditions of life. In England, the change in the milk when the cows are turned out to grass is usually said to be an increase in quantity, but with a lower fat content. Broadly speaking, it may be said that if the cows are sufficiently fed a change of food produces, at most, a temporary effect upon the quality of the milk.

Influence of season.—According to the numerous analyses of Richmond and Vieth‡ the winter's milk is richest, the summer's poorest, while milk in spring and autumn is of intermediate quality.

They found the average amount of fat to be at its maximum

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* Total cost of food, less value of obtainable manure.

† Assuming butter to contain 82·4 % fat and that 96·3 % of the total fat of the milk to be obtained as butter.

‡ Dairy Chemistry, 127.

(4·30 %) in November, at its minimum (3·79 %) in June; the solids not fat showed a maximum (8·92 %) in October and a minimum (8·71 %) in August.

Influence of time and manner of milking.—In most cases cows are milked twice a day—morning and evening. The intervals between the two milkings are usually unequal, being often 10 or 11 hours and 14 or 13 hours respectively. It is almost invariably found that the proportion of fat is distinctly greater in evening's than in morning's milk, and in some cases the difference is very great.

In the spring of 1900 the author made a large number of analyses of the separate milk of 17 cows kept at the Experimental Farm of the East and West Ridings of Yorkshire County Councils,* which showed that the proportion of fat in milk is subject to much greater variation and that the differences in the amount of fat in morning and evening milk, especially of cows yielding large quantities, are often greater than is usually stated.

The details are set out in diagrams, five of which are reproduced in Table I. The proportion of fat, it will be seen, in the milk of a cow, varies enormously from day to day; *e.g.*, consider the case of cow No. 1: On March 27th in the morning her milk contained 1·9 % fat, next morning she gave milk containing 2·7 %, while on the evening of April 7th 5·1 % fat was found. Table II. shows the maxima and minima for all the cows during the whole period. The invariably higher quality of the evening milk (the black line in Table I.) is also clearly shown. That full value may be obtained from a study of these diagrams it will be useful to give particulars of the cows whose milk was investigated:—

No. of Cow.	Age. Years.	Days since calving to April 1.	Weight in lb.	Tuberculin test indication.	Average milk yield. a.m. lb.	p.m. lb.
1	4	40	1204	Free	22	14
2	4	226	1148	Affected	8	5
3	4	244	1218	Doubtful	11	8
4	5	Calved April 2	980	Free	28	17
5	6	116	1352	Affected	18·5	14

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* Transactions of the Highland and Agricultural Society 1901, p. 218.

No. of Cow.	Age.	Days since calving to April 1.	Weight in lb.	Tuberculin test indication.	Average milk yield. a.m. lb.	Average milk yield. p.m. lb.
6	6	38	1196	,,	29	18
7	3	88	1008	,,	17	12
8	3	83	878	Free	15	10
9	5	30	1354	,,	20	15
10	3	Not milking	1354	,,	—	—
11	7	,,	1380	Affected	—	—
12	3	223	992	,,	15	8
13	4	221	1322	,,	10	6
14	3	157	1092	,,	15	10
15	4	154	1196	Free	19	12
16	4	154	1248	,,	13	8
17	4	14	986	,,	18·5	13
18	4	14	1008	,,	25	15
19	4	10	1036	Affected	24	17
Mean yield of whole herd ...				...	308	202

The investigation commenced with the evening's milk of March 22 and ended with the morning's milk of April 12, 1900. The cows were milked at about 6 a.m. and 3 p.m. Each cow received daily 3lb. cotton-seed meal, 3lb. maize meal, 3lb. bran, 2lb. wheat meal, and chaff and hay *ad lib.*

By milking several cows four times a day at intervals of six hours and analysing the milk the following figures were obtained:—

	Time of milking. 5 a.m. lb.	11 a.m. lb.	5 p.m. lb.	11 p.m. lb.
Percentage of fat in milk (mean)...	2·8	3·6	3·5	3·0
Weight of milk secreted (total) ...	40·0	23·5	24·0	24·0
,, ,, (ratio) ...	1·0	0·59	0·60	0·60
Weight of fat yelded (total) ...	1·1	0·85	0·82	0·70
,, ,, (ratio) ...	1·0	0·77	0·75	0·64

From these results it appears that the milk secreted between 5 a.m. and 5 p.m. is much richer in fat but smaller in quantity than that secreted at night, and that by far the largest amount is secreted in the six hours after 11 p.m. Other experiments

TABLE I.

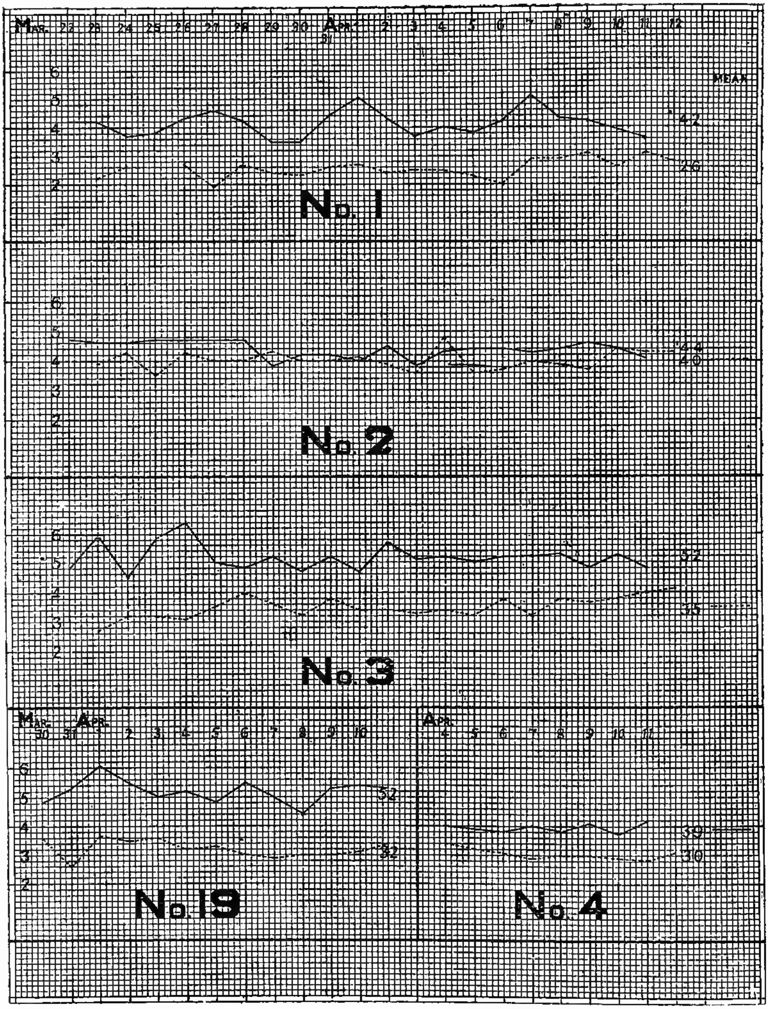

Table I. shows the variations in the amounts of fat in the milk of five of the cows. In each case the large figure gives the number of the cow, the dotted line the percentage of fat in morning's milk, the continuous line that in evening's milk of the same day. Each small division represents 0·2 per cent. of fat.

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TABLE III.

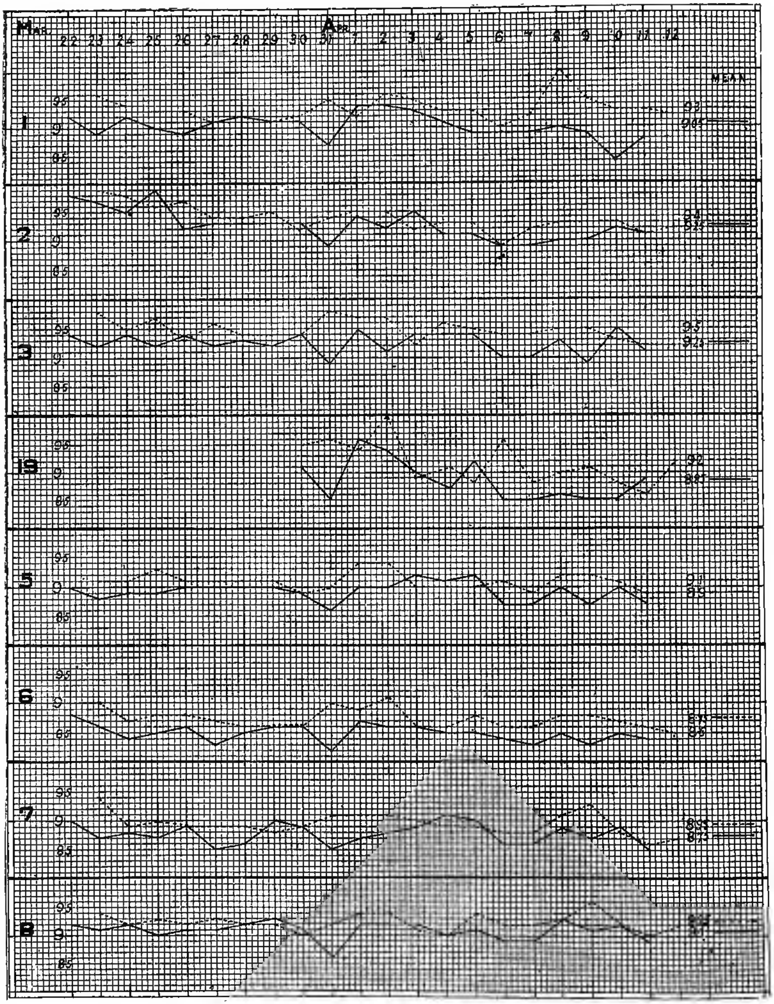
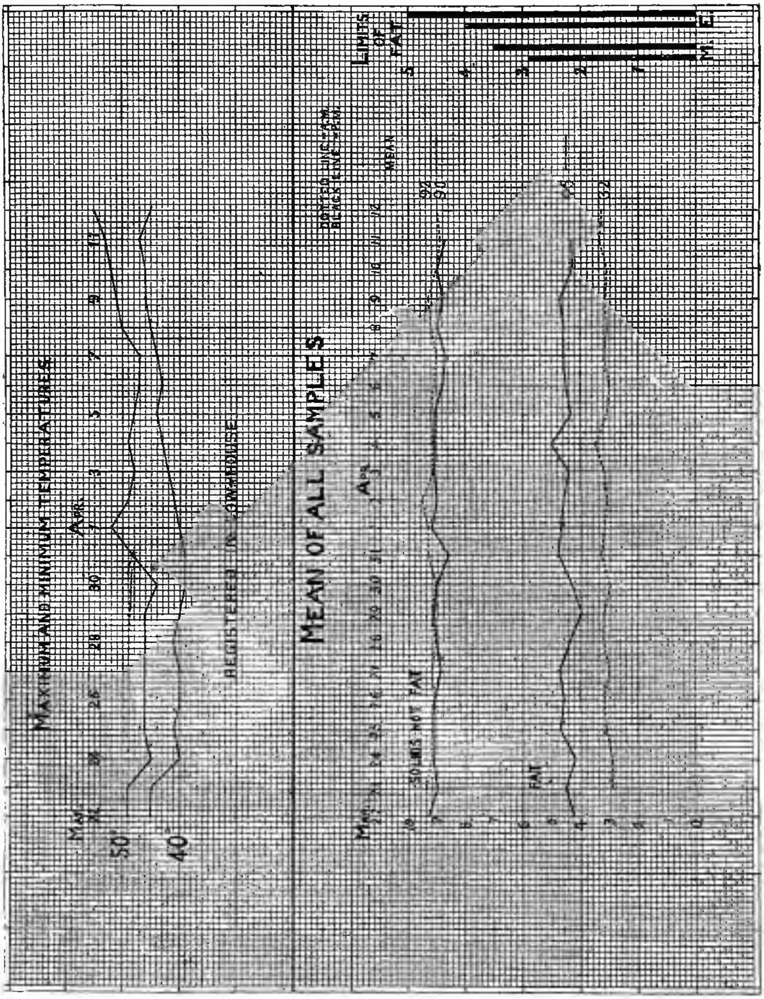


Table III. shows the variation in the amounts of solids not fat. The dotted line refers to the morning's milk, the continuous line to the evening's milk. Each small division represents 0·1 per cent. of solids not fat.

TABLE IV.



This fig. shows the variation in the highest and the lowest temperatures in the cow-house, and the daily mean of all the milk samples in percentages of fat and of solids not fat; also, on the right-hand side, the limits between which the daily mean percentage of fat was observed to vary.

agree with these results. It is also well known that the milk first drawn from a cow at milking time is very poor in fat ("fore milk"), while the last portion ("strippings" or "afterings") is very rich.. Cases in which the "fore milk" contains less than 0·5% of fat have been noticed, while "strippings" will sometimes contain as much as 10%. It is also found that the size as well as the number of fat globules per unit volume increases as the milking proceeds. This is probably due to a partial "creaming" taking place in the udder, since the production of milk seems to be a continuous process.

The solids not fat are liable to much less variation (*v.* Table III.). The average amount appears to be larger in morning's than in evening's milk.

It is probable that the proteids are subject to greater variation than the sugar. Indeed the last ingredient and also the ash appear to be remarkably constant in most cases.

Table IV. gives the mean values of the fat and solids not fat of the milk of the whole herd, and it will be noticed that much less variation is here shown.

The variations in the temperature of the cow-house are also given, but no distinct influence of temperature upon the composition of the milk could be detected.

THE MILK OF OTHER ANIMALS.—The following table gives the average composition of the milk of various mammals, mainly from analyses compiled by Richmond*:—

	Water.	Fat.	Sugar.	Proteids.	Ash.
Cow ...	87·10	3·90	4·75	3·40	0·75
Goat 1) (4) ...	86·04	4·63	4·22	4·35	0·76
Ewe(1) (4) ...	79·46	8·63	4·28	6·68	0·97
Buffalo(4) ...	82·63	7·61	4·72	4·14	0·90
Woman ...	88·20	3·30	6·80	1·50	0·20
Mare ...	89·80	1·17	6·89	1·84	0·30
Ass(2) ...	90·12	1·26	6·50	1·66	0·46
Bitch ...	75·44	9·57	3·09	11·15	0·73
Cat	81·63	3·33	4·91	9·08	0·58
Rabbit(4) ...	69·50	10·45	1·95	15·54	2·56
Camel ...	86·85	3·07	5·59	4·00	0·77

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* Dairy Chemistry, p. 323.

	Water.	Fat.	Sugar.	Proteids.	Ash.
Elephant(3) ...	67·85	19·57	8·84	3·09	0·65
Sow ...	84·04	4·55	3·13	7·23	1·05
Reindeer(5) ...	67·20	17·10	2·81	11·40	1·49
Porpoise ...	41·11	48·50	1·33	11·19	0·57
Whale ...	48·67	43·67	7·11		0·46

(1) See Voelcker, J.C.S. 1882, abst. 541; also Sartori, J.C.S. 1891, abst. 951.
(2) See Schlossmann, J.C.S. 1897, abst. ii. 574, who found much less fat.
(3) See Doremus, J.C.S. 1891, abst. 98.
(4) See also Pizzi, J.C.S. 1896, abst. ii. 120.
(5) Werenskiold, Expt. Stn. Record 1896, 713.

The constituents shown in the above table not only vary in amount but also in nature; the fat, particularly, differs in different animals. The fat of human milk, for example, is much poorer in volatile acids but richer in unsaturated acids than the fat of cows' milk. Laves[*] found in the fat of human milk only 1·4 % of volatile acids, including only a mere trace of butyric acid. The fat globules are smaller than in cows' milk.

Casein from different milks is also found to differ, especially in the manner of its coagulation under the influence of rennet or of acids.

The sugar of the milk of certain animals, too, apparently differs essentially from lactose, *e.g.*, the sugar in mares' milk is easily susceptible to alcoholic fermentation. According to Richmond, the milk of the gamoose, or Egyptian water buffalo, contains a sugar distinct from lactose.

MILK PRODUCTS.—Many valuable products are derived from milk, the most important being the following:—

1. Cream and skim-milk.
2. Butter and butter-milk.
3. Cheese and whey.
4. Condensed milk.
5. Koumiss.
6. Kephir.

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[*] J.C.S. 1894, abst. ii. 392.

Cream.—The fat globules of milk, being lighter than the liquid in which they are suspended, tend to separate and collect near the surface of the milk when the latter is allowed to remain motionless under the action of gravity. The rapidity with which the separation of the milk into two layers occurs—one rich in fat globules and the other almost devoid of them—depends upon many conditions. One of the most important is the size of the globules. The milk of Guernsey or Jersey cows quickly throws up its cream owing to the large size of the fat globules, while that of Ayrshire cows is slow in yielding cream.

Another factor of importance is the difference in the magnitudes of the forces acting upon the aqueous and fatty portions of the milk. Under ordinary conditions this (depending upon gravitation) is practically constant (though differing to a small extent according to the latitude); but, by imparting rapid rotation, centrifugal force of far greater magnitude than the force of gravitation, can be brought to bear upon the milk. The separation of the lighter fat from the heavier aqueous portion then becomes very rapid. This is the principle of the *milk separators* which are coming so rapidly into use. For details the reader is referred to any modern treatise on dairy work.

Another method of facilitating the separation of cream is known as "deep setting," in which the milk, while yet warm, is placed in cans about 18 inches deep, which are then surrounded with cold water or, better, ice. In this case the whole of the fat will be found on the surface after about 12 hours.

It is not quite easy to understand why the fat globules should collect at the surface more quickly when the milk is thus cooled than under ordinary conditions. As fat contracts and expands with changes of temperature more rapidly than water, a low temperature would tend to lessen the buoyancy of the fat globules, and on that account tend to lengthen the time necessary for their coming to the surface.

The writer is of opinion that the explanation of the action observed is to be found in the gentle convection currents which are set up by the cooling action of ice or water on the walls of the can. The milk in contact with the walls of the vessel as it cools becomes heavier and slowly sinks to the bottom, the warmer and therefore lighter milk rising in the more central portion of the vessel to make way for it, while the milk nearer the surface is slowly drawn outwards towards the walls of the vessel and sinks. In this way a very slow circulation probably takes place, and during the whole time the fat globules are tending to rise to the surface, from which, on account of their levity, they will not be moved by the gentle downward currents. In this way the fat globules accumulate quickly at the surface, behaving in much the same way as if the milk were set in a very shallow vessel, the buoyancy of the globules having, so to speak, only to do the work of raising them out of the slow current of milk which is continually passing beneath the cream layer. Another factor which may aid in the process is the persistence of the fat during rapid cooling in its liquid, and therefore lighter, form, while the aqueous portions of the milk are rendered denser as they cool. As has already been stated, liquid fat is of lower specific gravity than solid fat at the same temperature, and there is some evidence that super-cooling of fat globules readily occurs. In ordinary setting, assuming that the same period elapses before the fat solidifies, the aqueous portion of the milk will not differ so much in density from the fat globules for so long a time as when the milk is quickly cooled.

Another possible way in which the quick cooling facilitates the rise of the fat may be in its preventing or delaying the coagulation of the small quantity of fibrin which, according to Babcock, is present in milk and which by entangling the fat globules hinders their rise under ordinary conditions of setting.

Many other advantages attend the practice of cold setting, among which the very important one of lessening the fermentation of the milk sugar and of hindering all bacterial growth, both in the cream and in the skim milk, by the low temperature and shorter time of setting, may be mentioned.

The composition of cream is liable to enormous variation, the proportion of fat fluctuating between 9 or 10% and 60 or even 70%.

If obtained at low temperature the amount of fat is usually low—about 20%; by shallow setting it may vary from 15 to

40 %; whilst with the separator, by adjusting the rate at which the milk passes away, almost any richness of cream may be obtained.

The aqueous portion of cream contains the usual solids of milk almost in the same proportion as in milk itself. The amount of solids not fat is usually slightly higher than in milk, due probably to evaporation of water during the setting. This is especially the case with "clotted cream," prepared by the Devonshire method, and whose composition is more uniform than that of ordinary cream. According to Richmond the average composition of this substance is—water 34·26 %, fat 58·16, ash 0·60, solids not fat 7·52.

The specific gravity of cream can only conveniently be determined directly if its fat is below 30 %. If stiffer than this it must be diluted with an equal volume of separated milk and the specific gravity of the mixture taken. Richmond gives the following numbers:—

Specific gravity.	% fat.	Specific gravity.	% fat.
1·0035	29·0	1·0125	21·3
1·0070	26·0	1·0130	20·8
1·0090	24·0	1·0210	13·5

—and he gives as a formula connecting the specific gravity and percentage of fat in cream the following:—

$$F = 32{\cdot}0 - 0{\cdot}892\,\frac{G}{D},$$

where F = per cent. of fat, G = lactometer reading (*i.e.*, specific gravity × 1000 − 1000) and D = true specific gravity.

This formula does not apply to clotted cream.

Skimmed Milk is of course similar in composition to ordinary milk, with the exception of containing little or no fat. The other constituents—water, sugar, casein, &c.—though preserving the same ratio to each other, are slightly raised in percentages. Skimmed milk from shallow setting usually contains anything between 0·4 and 2 % of fat, while with a good separator the amount is usually from 0·05 to 0·3 %. Its specific gravity is usually between 1·034 and 1·037. Its average composition as given by Fleischmann is—

	Setting.	Separator.
Water ...	89·85	90·30
Fat	0·75	0·25*
Proteids ...	4·03	4·00
Milk sugar ...	4·60	4·70
Ash	0·77	0·75
	100·00	100·00

Butter is produced by agitating or "churning" milk, or more generally cream, until the fat globules coalesce. The resulting semi-solid mass which separates from the butter-milk consists largely of completely continuous fat, a few of the original globules, however, remaining. Under the microscope many spherical globules are visible, which, according to recent observations, consist of minute drops of enclosed butter-milk or water and not of fat.

The effect of churning is purely mechanical; the fat globules are by violent motion knocked together and adhere, thus giving rise to larger, irregular masses, which in turn collide together or with other fat globules. In this way the masses of fat gradually increase in size, portions of the aqueous liquid becoming enclosed during their formation. At first the increase in size of the fat particles and their irregular shape give rise to increased viscosity (this phenomenon is sometimes known as "going to sleep"); but as they grow larger they tend to separate more completely from the butter-milk and float, the contents of the churn becoming mobile. The butter grains are then, by working, pressed together, and more and more of the butter-milk is separated from the fat. In order that the amount of liquid retained by the butter may be small, it is necessary that the temperature should be carefully adjusted. The optimum temperature, however, depends partly upon the temperature at which the cream has been for some time prior to the churning and the rapidity with which it has been raised or lowered. Richmond gives the following as most suitable:—

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* In the author's experience, separated milk generally contains much less fat than this. With good management probably not more than 0·1 % of fat should be left in the separated milk.

Recently separated cream (quick churning)...	8° C.
,, ,, ,, (slow churning) ...	13° C.
Sour cream (in summer)	13° C.
,, ,, (in winter)	18° C.

Fleischmann recommends 13° for sweet cream, 16° for sour cream.

If churned at too high or too low a temperature the butter contains a higher proportion of water. According, however, to American experiments, the optimum temperature for churning varies with the breed of cows and also with their food, being higher when cotton seed or cotton-seed meal is used. It seems to be generally admitted that "ripened," *i.e.*, sour, cream, gives a higher yield of butter and churns more readily than sweet cream.

Opinions greatly differ as to the relative quality of butter from sweet and from ripened cream, but it is generally agreed that the best flavour and aroma in butter can only be obtained from the use of properly ripened cream *(v. infra)*, though disagreeable flavours are also liable to be produced owing to the products of undesirable micro-organisms. Moreover, if the cream be very sour, and especially if it be sour before removal from the milk, the resulting butter will contain a large amount of casein, and on this account probably will more readily become rancid.

Salt is usually added to butter both as a condiment and also to check decomposition. The amount used varies greatly, from a mere trace up to 7% being found.

It is difficult to give any average composition of such a variable product; usually it varies between the following limits:—

	%
Fat	78·0 to 94·0
Water	5·0 to 16·0
Casein	0·5 to 3·0
Ash	0·1 to 4·0
Sugar	0·2 to 0·7

The butter from ripened cream is usually richer in casein and water than that from fresh cream. It is generally stated that salt butter contains a higher proportion of water than fresh, but according to Richmond this is not so; although salt butter appears to be wetter and on being cut allows brine to flow out, thus giving it a wet appearance, the amount of water is said by Richmond to be less on the average than in unsalted butter.

"Pickled" butter, however, made by warming butter and kneading it with brine, may contain a very high percentage of water. Sixteen per cent. of water is usually taken as the upper limit in good butter, though this may be exceeded by Irish "pickled" butter.

The following table gives the average results of the analyses of various kinds of butter by Vieth:—

	Fat.	Water.	Curd.	Salt.
English ...	86·85	11·54	0·59	1·02
French, fresh ...	84·77	13·76	1·38	0·09
,, salt ...	84·34	12·05	1·60	2·01
German ...	85·24	12·24	1·17	1·35
Danish ...	83·41	13·42	1·30	1·87
Swedish ...	82·89	13·75	1·33	2·03

Butter is sometimes made—*e.g.*, in certain districts in Ireland and in Scotland—by churning whole milk. In all cases the milk is allowed to go sour first, and the character of the butter produced is very variable. The yield of butter is said, on the average, to be higher than that from sour cream by the old setting method, but less than that from sour separated cream.

Butter-milk resembles skim-milk in composition, but has a peculiar flavour of its own and is generally acid. Its fat content varies considerably and is usually less with ripened than with fresh cream. The fat also varies according to the efficiency with which the churning has been performed.

Its composition will probably be between the limits—

	%
Water	89·0 to 91·0
Fat	0·3 to 3·5

	%
Sugar	4·0 to 5·0
Proteids	3·3 to 4·0
Ash	0·7 to 0·8

The losses of fat in butter-making occur in the skimmed milk, in the butter-milk, and in mechanical loss of butter. In American stations the loss varied from 7 to 25%. When the separator was not used the loss was greatest with Ayrshire and Holstein cows and least with Guernseys and Jerseys.

Cheese is formed from milk by coagulating the casein, which entangles and carries down with it the greater portion of the fat, while the sugar, albumen, and a portion of the casein remain in the whey.

The coagulation of the casein may be brought about, as already described, either by acids or, more usually and with a better product, by rennet. The curd after separation from the whey is pressed and allowed to "ripen," a process somewhat obscure, but probably dependent upon micro-organisms.

The composition of both curd and whey will naturally vary with that of the milk from which they are formed, whether this be whole milk, skim-milk, or enriched by the addition of cream.

The curd and whey from whole milk have the following average composition:—

	Curd %.	Whey %.
Water	50·0	92·94
Fat	26·7	0·35
Sugar	2·3	5·10
Casein	20·0	0·46
Albumin	trace	0·46
Ash	1·0	0·69
	100·0	100·00

The character of the curd produced depends largely upon the temperature at which the rennet is introduced, also upon the acidity of the milk.

As already stated, rennet acts most rapidly at about 37° (or

40° according to Fleischmann), and if the milk be about this temperature the curd is firm and hard, while milk at low temperatures or at about 50°, yields soft curd. The more acid the milk the more rapid is the action of rennet.

In some cases cheese is made without rennet, by simply allowing the milk or cream to turn sour and thus bring about the coagulation of the casein. This method is chiefly used for the preparation of cream cheese.

Soft cheeses are made by coagulating with rennet at a low temperature (about 25° to 30°). They always contain a considerable quantity of water. Brie, Camembert, and Neufchâtel are types of this class.

Hard cheeses are formed when the coagulation takes place about 35°

The quality of a cheese largely depends upon the amount of fat in it. Some hard cheeses are made from *enriched milk, i.e.*, milk to which additional cream has been added. Stilton cheese is an example.

From *whole milk*, Cheddar, Cheshire and Wensleydale, Gruyère, Edam, and Gorgonzola cheeses are made.

From *mixtures of whole milk and skimmed milk*, Gloucester, Leicester, and (sometimes) Cheddar, also Parmesan and (often) Edam cheeses are derived.

From *skimmed milk*, various poor cheeses, *e.g.*, Limburg and Danish, are produced, but are of little value or importance.

Roquefort cheese is made from sheep's milk, as are several other varieties.*

The general practice in making a cheese is to hasten the ripening of the milk by the addition of a "starter," consisting of sour milk containing large numbers of the lactic bacterium, or a pure culture of the lactic ferment. When lactic fermentation has proceeded far enough, *i.e.*, when the proportion of lactic acid in the milk reaches a certain amount (determined most safely by titration with standard soda solution, and often about 0·2% lactic acid) it is ready for curdling. By trial with a small quantity of the milk at about 30° the amount of rennet required to cause coagulation in the desired time is then determined, and this quantity is then added to the main mass.

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* Sartori, Jour. Chem. Soc. 1891, abst. 951.

If the cheese be wanted to cure rapidly, the rennet should cause coagulation in about 20 minutes; if a slow curing be desired, in about 40 minutes. When the curd is solid the temperature is raised to about 37° and kept constant until a hot iron placed in contact with the curd and drawn away pulls off threads about half an inch in length. This usually occurs in about one or two hours after the milk is heated to 37°.

The whey is then run off and the curd stirred and turned to allow the whey to escape. The curd is next reduced in a mill, salted, and pressed in moulds. The cheeses are then stored away at a temperature of 15° to 18° and allowed to ripen.*

The changes which occur during ripening are little understood, although recently an enormous number of researches have been made on the subject. Considerable loss of water occurs, the milk sugar of the whey left adhering to the curd is converted into lactic acid, but the most obscure changes are those which affect the proteid matter.

The original casein is converted into other more digestible and palatable nitrogenous bodies, consisting probably of peptones and albumoses. Exactly how these changes are brought about is still a matter of uncertainty.

Freudenreich† asserts that the lactic bacteria are able to decompose casein and thinks that these organisms play the most important part in the ripening of cheese. This view has been supported by the investigations of Lloyd‡ and Campbell§. On the other hand, Babcock and Russell announced in 1897 the discovery of a proteolytic enzyme or unorganised ferment, to which they have given the name *galactase* and to which they ascribe the chief share in the ripening of cheese. This enzyme is present in the milk of all animals, possesses the power of peptonising casein, and in many respects resembles trypsin, the enzyme of the pancreatic juice. It is more active in alkaline than in acid solutions. By its action on casein, albumoses, peptones, amides, and ammonia are formed.|| Freudenreich has repeated and confirmed Babcock and Russell's experi-

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* For a detailed account of Cheddar cheese making see a Report by Lloyd, published by the Board of Agriculture, 1899.

† Landwirtschaftliches Jahrbuch der Schweiz, 1897; also 1898, 279.

‡ Board of Agriculture, Report on Cheddar cheese making, 1899.

§ Transactions of the Highland and Agric. Society of Scotland, 1898.

|| Jour. Chem. Soc. 1900, abst. ii. 712.

ments.* He finds that formalin or a temperature of 75° weakens the action of galactase.

Duclaux, as long ago as 1880†, ascribed the ripening of cheese to changes in the casein produced by enzymes, but the latter were thought by him to be produced by the life-processes of micro-organisms. It seems probable that this view is also true so far as some of the changes in cheese are concerned.

The following are analyses of several varieties of cheese quoted by Wiley‡:—

	Water. %	Casein. %	Fat. %	Sugar. %	Ash. %
Cheddar ...	34·4	26·4	32·7	2·9	3·6
Cheshire ...	32·6	32·5	26·0	4·5	4·3
Stilton ...	30·4	28·9	35·4	1·6	3·8
Brie ...	50·4	17·2	25·1	1·9	5·4
Neufchâtel ...	44·5	14·6	33·7	4·2	3·0
Roquefort ...	31·2	27·6	33·2	2·0	6·0
Edam ...	36·3	24·1	30·3	4·6	4·9
Swiss ...	35·8	24·4	37·4	—	2·4
Cream ...	38·6	25·4	30·2	2·0	4·0

The above analyses are of the type usually made, but are not satisfactory, inasmuch as they do not differentiate between the various nitrogenous compounds present, some of which are almost valueless as food. Recently attempts have been made to get more detailed results.§ As an example, Stutzer gives the results of his investigation of the nitrogenous constituents of Camembert and of Swiss cheeses as follows; the total nitrogen in each was distributed thus:—

	Camembert. %	Swiss. %
Nitrogen as ammonia ...	13·0	3·7
,, ,, amides	38·5	9·0
,, ,, albumoses, peptones	30·5	8·6
,, indigestible	4·0	2·4
,, as casein, albumin ...	14·0	76·3

In the Camembert the ripening process had proceeded very far, while the Swiss cheese was comparatively fresh.

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* Jour Chem. Soc. 1900, abst. ii. 712.

† Jour. Chem. Soc. 1882, 436.

‡ Agricultural Analysis, Vol III. 524.

§ Stutzer, Jour. Chem. Soc. 1896, abst. ii. 683.

Condensed Milk.—This is milk which has been concentrated by evaporation in a partial vacuum (so as to perform the operation at a low temperature) and to which sugar, either cane sugar or sometimes glucose, has been added. The extent of the concentration is usually to about one-fourth the original bulk. Sometimes no sugar is employed, but generally about one pound is added to each gallon of milk.

Whole milk and separated milk are both employed in the manufacture of condensed milk.

The composition of various forms is usually about—

	Water. %	Fat. %	Milk sugar. %	Cane sugar. %	Proteids. %	Ash. %
Sweetened, from whole milk ...	25	11	14	37	10	2
,, ,, skim-milk ...	29	1	15·5	40	11	2·5
Unsweetened, from whole milk	62	11	14	—	10	2

They are generally recommended to be mixed with from five to seven volumes of water. The resulting mixture is obviously much poorer in fat and proteids than genuine milk.

Koumiss is an alcoholic beverage produced from milk by fermentation. As already stated, lactose does not readily undergo alcoholic fermentation. The sugar of mares' milk, however, readily ferments, and an alcoholic liquid can be prepared by the addition of a little koumiss, or even sour milk, to mares' milk. Such beverages have been long known in Tartary.

By the addition of a small quantity of cane sugar and yeast to cows' milk a similar beverage can be prepared.

The casein at first coagulates, but afterwards partly redissolves, and does not appear to be so liable to coagulation under the influence of gastric juice as is that of fresh milk. Koumiss is thus very easily digested and acts both as a stimulant and as a food; it is therefore used for invalids.

The following analyses of koumiss are given by Wiley:—

	Water. %	Sugar. %	Alcohol. %	Fat. %	Proteid. %	Carbon dioxide. %	Acidity. %
From cows' milk	89·32	4·38	0·76	2·08	2·56	0·83	0·47
,, mares' ,,	91·87	0·79	2·89	1·19	1·91	—	1·04

The acidity is expressed in terms of lactic acid. The proteids are partly casein, but also consist of albumoses. The carbon dioxide gives an effervescent character to the bottled koumiss.

Kephir is a similar product made in the Caucasus from cows' milk. The "kephir" grains which are used to start the fermentation are evidently impregnated with micro-organisms and are placed in the milk until fermentation commences. After this they are dried and kept for future use. Their origin appears to be unknown. Many organisms have been found in kephir grains, including bacteria and yeasts. It has been stated that the kephir contains an enzyme—*lactase*—which has the power of hydrolising milk sugar, thereby producing glucose and galactose, and that yeast then attacks the former as in ordinary alcoholic fermentation.

Kephir resembles koumiss in composition, but contains less alcohol and albumoses and more casein.

MILK PRESERVATION.—Milk is peculiarly liable to undergo change under the influence of micro-organisms, for the growth of which it serves as an excellent medium. In the udder, milk is normally free from micro-organisms, but, unless special precautions are taken, within a very short time after milking it absolutely teems with them.

In many cases examined, milk within a few minutes of milking has been found to contain thousands of organisms per cubic centimetre. The organisms, or their spores, are derived from the air, the hands of the milker, the hair or teats of the cow, and particularly from the vessels in which the milk is received.

The rate at which the bacteria multiply is largely dependent upon the temperature. It was found that after fifteen hours at 15°, milk contained 100,000 bacteria per cubic centimetre, while the same milk kept fifteen hours at 25°, contained 72,000,000 per cubic centimetre, and at 35°, 165,000,000 per cubic centimetre.*

The importance of quickly cooling milk is thus evident, since usually it is desirable to hinder as much as possible the growth of bacteria. The micro-organisms which find their way into milk are of various types; in most cases, perhaps, the majority are such as convert milk sugar into lactic acid, while organisms of almost all kinds may be found, many objectionable and some highly dangerous. The first evident effect of the growth of the organisms is usually the souring and consequent curdling of the milk.

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* Miquel, Central-B. für Agricult.-Chem. 1890, 575.

It is obvious, therefore, that if the milk is to be kept for any length of time some means of preventing the growth of these organisms must be taken. Two chief methods suggest themselves: (1) To prevent the entrance of the germs, or (2) to use some means which will either kill them or prevent their growth.

The first method is almost impracticable on the large scale, but the second is often adopted. This is either by "sterilisation" or "Pasteurisation."

In the former process the milk is heated to a sufficiently high temperature (about 115° C.) to destroy all germs. This is usually effected in steam under pressure. The milk is then kept excluded from the air, or air which has filtered through a thick layer of cotton wool may be admitted. Milk so prepared will not sour and may be kept indefinitely. Unfortunately certain undesirable changes are produced in the milk by this treatment. The taste and smell are altered, a portion of the calcium citrate and the albumin are precipitated, and the casein (probably by the precipitation of the calcium compounds) becomes much less coagulable by rennet. Moreover, the milk becomes brown, and the enzyme originally present in the milk and which has the power of giving a blue colouration with hydrogen peroxide and para-phenylene diamine, $C_6H_4(NH_2)_2$, is destroyed. The fat rises much less readily, and the cream layer, though very thin, is richer in fat than ordinary cream, containing often over 40% instead of 20 to 30% as in the case of fresh cream.

In Pasteurising, a lower temperature—about 60° or 80°—is employed, and the milk is subjected to this two or three times, with intermediate cooling. The taste and properties of the milk are not so much altered by this treatment, but the albumin is changed, so that practically all of it is precipitated along with the casein on the addition of salts, *e.g.*, magnesium sulphate. The casein, when precipitated from sterilised or Pasteurised milk, is much more finely divided than that from fresh milk. It is therefore probably more easily digested, especially by young children.

The chief difference between human milk and cows' milk is in the character of the curd which is produced by rennet or the gastric juice of young children; the former yields a finely divided mass, while the latter gives a closely adherent, heavy clot, probably much less easily digested. This difference is ascribed, not to a difference in the casein or even in its amount, but to the different amounts of calcium present. Human milk contains about 0·03% CaO, while in cows' milk there is about 0·16% CaO. It has been shown that the coagulation of casein by rennet is dependent upon the presence of calcium compounds and that in their absence no coagulation occurs.* Hence it has been proposed to render cows' milk more like human milk, and therefore more suitable for feeding infants, by the removal of a portion of the lime ("humanised milk"). This, it is said, can be done by adding about 0·5% of sodium citrate. The addition of lime water, it may be noted, though it delays curdling by reason of its alkalinity, would not improve the character of the curd when it is formed. Another somewhat curious fact is that cows' milk contains more lime than an equal volume of lime water (which contains about 0·13%), so that the idea that the addition of lime water aids in supplying materials for the formation of bone is founded on a misconception.

Other Methods of Preserving Milk.—As already stated, it is possible to prevent the growth of micro-organisms in milk by the addition of antiseptics, and this is often practised, especially in hot weather, when their growth is apt to be very rapid. The chief antiseptics employed in preserving milk, butter, and cream are—

Boric acid or *borax*, H_3BO_3 or $Na_2B_4O_7.10H_2O$.
Salicylic acid, $C_6H_4(OH)COOH$.
Formaldehyde, H_2CO, generally as "Formalin."

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* Arthus and Pagès, 1890.

The use of preservatives of any kind is probably not a wholesome practice, for though the growth of most of the micro-organisms is prevented, all change is not stopped. Moreover there is considerable probability that, with children particularly, the use of preservatives is attended with danger to digestion. Many of the substances used as preservatives have been shown* to have an injurious action upon digestive enzymes.

Sodium carbonate or bicarbonate is sometimes added to milk as a preservative. In reality it does not thus act, but merely prevents the lactic acid, formed by fermentation, from coagulating the casein, and by neutralising the acid as fast as it is formed, probably aids the change of the sugar into lactic acid.

Milk as a Medium for the Spread of Disease.—Milk is peculiarly well fitted as a nutrient for the growth of micro-organisms. As has already been stated, the number of organisms present in ordinary samples is enormous. Fortunately the majority of these bacteria are harmless so far as their effect upon health is concerned, but unfortunately milk very readily acts as a conveyer of pathogenic organisms.

Diphtheria, scarlet fever, typhoid, and especially tuberculosis† have been in many instances communicated by milk. Careful Pasteurisation of all milk is greatly to be desired, and already dairies are being started in various parts of England in which the milk is submitted to a modified Pasteurisation. The milk is heated in bulk to a temperature of 60° to 65° and maintained at this temperature for 20 minutes, then quickly cooled and sent out to the consumer, best in closed glass bottles. Russell has lately shown that the tuberculosis bacillus may be destroyed by heating to 60° for 20 minutes, provided the milk is heated under such conditions (with constant agitation and in a closed vessel) as to prevent a pellicle forming on the surface.‡ The advantages of using a low temperature in Pasteurising have already been indicated. Milk Pasteurised at 60° cannot be distinguished by taste from untreated milk, and though the rise of the cream is rendered slower, the soluble albumin of the milk is hardly diminished.

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* Leffmann, Jour. Franklin Instit. 1899, 97.

† It has recently been asserted that bovine tuberculosis is probably not communicable to man; but, though the opinion is that of the great authority, Koch, it is not yet generally accepted.

‡ *v. The Times*, Feb. 25th, 1901.

By one treatment of this kind the milk is not completely sterilised, but the pathogenic organisms are probably entirely destroyed and the keeping qualities of the milk greatly improved.

CHAPTER XV.

The Analysis of Milk and Milk Products.

For a detailed account of the methods employed in making a complete analysis of these substances the reader must consult a manual on analysis. Only a few of the more important determinations in the analysis of milk, butter, and cheese will be described here.

MILK.—For many purposes an examination of milk directed to the estimation of the percentages of total solids and fat and the absence or presence of preservatives is sufficient.

The Amount of Fat, as already stated, is subject to greater variation than that of the other constituents, and from a practical standpoint is usually considered the most important criterion of the value of a sample.

Of many methods which have been described the following are among the most reliable and best known :—

1. *Adams's paper-coil method.*—In this process 5 c.c. of the milk are allowed to run from a pipette upon a strip of filter paper (from which all matter soluble in ether has previously been removed) about 22 inches long by 2 inches wide. The paper is then dried by holding it near a fire, care being taken not to scorch it. It is then rolled into a coil round a short piece of wide glass tubing sealed up at each end (containing a little mercury so that it may not float in ether)* and introduced into a Soxhlet extractor, in which it is repeatedly treated with ether, the ether with the dissolved fat being received in a wide-mouthed small flask, previously weighed. After eight or ten siphonings the flask is removed from the extractor, the ether distilled off into another condenser, the flask dried in the steam bath for an hour or so, cooled, and weighed. The

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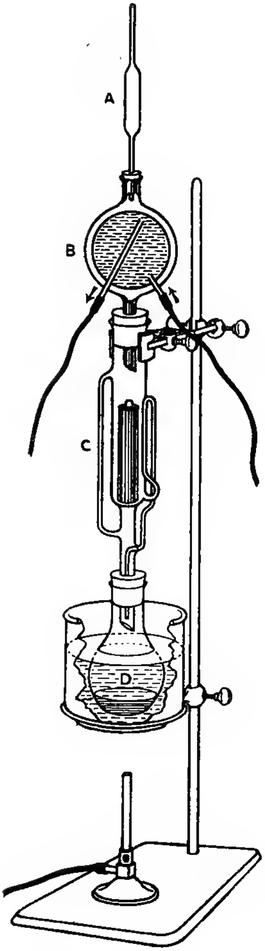
* This device greatly hastens the extraction, by diminishing the amount of ether required to fill the apparatus.



A is a pipette which acts as a condenser to the ether vapour which may escape condensation in B.
B is the metal ball condenser.
C is the Soxhlet extractor containing the coil of paper and the glass bulb as core.
D is the weighed flask, in a metal water bath.

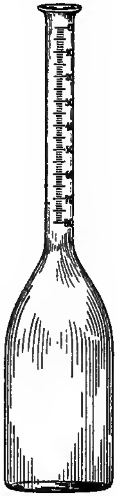
increase in weight of the flask is taken as fat. The percentage is then calculated, knowing that the weight in grammes of milk taken = 5 × sp. gr.

In this, as in all operations in which ether is employed, great care should be taken to avoid ignition of the heavy ether vapour. The most convenient condenser to use with the Soxhlet extractor is the form consisting of two concentric metal spheres, the inner one kept cool by a stream of cold water and the vapour passed into the narrow space between the spheres. This method of estimating fat is one of the most accurate, especially if *dry* ether be used.

2. *Werner-Schmid method.*—This process, requiring only very simple apparatus, is especially suited for sour milk. 10 c.c. of the milk are placed in a large test tube ("boiling tube") or, better, a 50 c.c. stoppered graduated test mixer; 10 c.c. of strong hydrochloric acid are added and the mixture shaken and heated in a water bath for about 10 minutes until a brown colouration is produced. The whole is then cooled and 30 c.c. of water-saturated ether are added. The vessel is then closed, vigorously shaken so as to dissolve the fat, and then allowed to stand until the ether separates as a clear layer. The volume of the ethereal layer is then read off and 10 c.c. are withdrawn by means of a pipette, run into a small weighed flask, the ether distilled off, the flask dried in a steam bath, cooled, and weighed. The greatest drawback to this method is the formation of a flocculent, semi-solid layer between the clear ethereal and aqueous portions in the test mixer, which renders the reading of the volume of the ether difficult.

3. **Rapid Centrifugal Volumetric Methods.**—Several methods have been devised in which a measured quantity of milk is treated with acids so as to dissolve the casein, &c., heated, and subjected to centrifugal force so as to bring about the separation of the fat in a fluid state, the volume of which is then read off and thus its percentage amount. These methods are very rapid, easy to carry out, and sufficiently accurate for most purposes. The best known of the modern methods are—

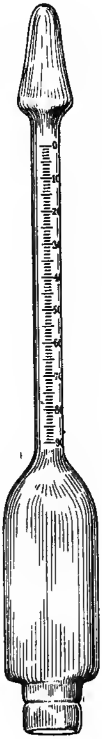
(a) *The Leffmann-Beam process.*—In this process the milk is mixed with a small quantity of a mixture of amyl alcohol, $C_5H_{11}OH$, and hydrochloric acid, whereby the casein is coagulated. Strong sulphuric acid is then added, in which the casein dissolves, the whole liquid becoming hot from the action of the sulphuric acid upon the water. The amyl alcohol aids in the separation of the fat, most probably because it is a common solvent for fat and the acid liquid. The emulsified fat thus speedily separates and by centrifugal action forms a distinct and clear layer above the acid liquor, which usually takes a dark purple colour. The operation is carried out in small flask-like vessels provided with narrow graduated necks, and the separation of the fatty layer is effected by a centrifuge driven by toothed gearing. The mode of performing the test may briefly be described thus: 15 c.c. of milk are run into the vessel from a pipette, 3 c.c. of a mixture of equal volumes of amyl alcohol and strong hydrochloric are then added and the whole shaken. 9 c.c. of sulphuric acid of specific gravity 1·835 at 15° C. are then run slowly into the vessel with frequent mixing; the mixing is best done by rotating the flask in the hand, care being taken to avoid loss of the contents and also



Leffmann-Beam flask. One-half natural size.

the accumulation of the heavy acid at the bottom of the vessel. In the latter case excessive darkening or even charring of a portion of the milk may occur and the test is spoiled. The whole liquid should become nearly transparent, though dark purplish in colour. The little flask is then filled with a hot mixture of equal volumes of strong sulphuric acid and water. It is then whirled for two or three minutes in the centrifuge, the handle being turned at the rate of about 80 to 100 revolutions per minute. The length of the fat layer is then read off and gives, without calculation, the percentage of fat in the milk. In reading off the fat it will be found convenient to use a pair of ordinary dividers, the legs of which are so adjusted that one is at the lowest part of the meniscus of the upper surface of the fat, while the other is at the point where the fatty layer touches the acid. The dividers are then placed so that one leg is at the zero of the scale, when the position of the other one on the scale will give, at once, the percentage of fat present.

(b) *The Gerber method.*—This method, which is very popular, is similar in principle to the last mentioned. The essential differences are in the apparatus used. Instead of open, flask-like vessels, corked tubes are used and the centrifuge is of simpler construction, being driven either by a string or strap, and running freely on ball-bearings, or by a steam, electric, or water motor. The materials employed are 11 c.c. of the milk, 1 c.c. of amyl alcohol, and 10 c.c. of sulphuric acid of specific gravity 1·825 at 15° C. The process is conducted in much the same way as with the Leffmann-Beam apparatus; it is generally necessary to keep the tubes warm by external heat. This can conveniently be done by means of a Bunsen burner or spirit lamp placed under the centrifuge itself during rotation. A hot-water bath, often recommended, is not so good, because of its tendency to loosen the rubber stoppers; if they come out, the contents of the tube escape and the determination is spoiled. A white solid often separates out during the whirling of the tube and is found afterwards adhering to the cork and bottom of the tube. A quantity of this white powder was collected by the author in the autumn of 1901, washed thoroughly, dried, and examined; it was found to be calcium sulphate. Its formation furnishes a somewhat striking proof of the large amount of calcium compounds present in cows' milk.



Gerber tube. One-half natural size.

These rapid centrifugal methods have repeatedly been compared with the gravimetric processes for fat determinations, and the results have always proved to be in close agreement; the error being rarely more than 0·1 %.

Determination of Total Solids.—The principle of all the methods is simply to expel water by heat from a known amount of milk and determine the weight of the residue.

Direct evaporation of milk in a dish is slow and difficult owing to the formation of a skin, consisting mainly of proteids, upon the surface; this skin, or pellicle, is tough and impervious and interferes with the evaporation of the liquid below it. Many methods for avoiding the formation of the pellicle have been devised. One of the best is the following:—

A platinum dish containing about 10 grammes of recently ignited sand and a short piece of glass rod is weighed; 10 c.c. of milk are then run into it from a pipette. The dish is then placed on a water bath and the sand and milk stirred repeatedly, at intervals, until the mixture is apparently dry. Two hours further heating in a water bath or, better, in an air bath at 105°—110° is then generally sufficient to drive off all moisture. The dish is then cooled in a desiccator and weighed.

Determination of Specific Gravity.—This is usually performed by means of a modified hydrometer known as a "lactometer," the graduations usually ranging from 0 to 40, the reading of the instrument, sometimes known as "lactometer degrees," really giving the amount by which the density of the milk exceeds 1000 when the density of water is taken as 1000. Thus 0 on the lactometer scale would be the point to which the stem sinks in pure water, while 40 would be the point to which it sinks in a liquid whose specific gravity is 1·040 (water = 1) or 1040 (water = 1000). The lactometer, though easy and convenient to use, is not capable of great accuracy.

A specific-gravity bottle holding 25 or 50 c.c. affords much greater accuracy, though a determination requires more time. It will be found most convenient to determine the weight of the empty bottle and of the bottle filled with distilled water at a temperature slightly higher than the average temperature of the room and to use these values always. In any particular case, then, only one weighing—that of the bottle filled with milk at the temperature used before—is necessary. A more rapid and very accurate method of determining the specific gravity of milk is by means of the "Westphal balance."

It has been found that the specific gravity, total solids, and fat of a sample of cows' milk are related to each other in such a manner that it is possible to calculate the value of any one of these three quantities if the other two are known. This can be done because an increase in the solids not fat produces a rise in the specific gravity, while the more fat there is present the lower will be the specific gravity. Many formulæ have been devised to facilitate the calculation. One of the most convenient is that of Richmond:—

$$T = 1{\cdot}2F + 0{\cdot}25G + 0{\cdot}14,$$

where

T = percentage of total solids.
F = percentage of fat.
G = "lactometer degrees" (*i.e.*, sp. gr. × 1000 − 1000).

The results obtained for total solids from the fat and specific gravity by this formula agree closely with actual determinations.

Determination of Proteids.—The total amount of albuminoids in milk can most easily be deduced from the amount of total nitrogen. This is conveniently done by the Kjeldahl method described on p. 94. From 5 to 10 grammes of milk are taken and 20 or 25 c.c. pure sulphuric acid, the rest of the process being performed as already described in the case of soils. By multiplying the total nitrogen by 6·38 the total proteids are obtained, since both casein and albumin contain 15·7 % of nitrogen.

If separate determinations of the amounts of casein and albumin be required, the casein must be precipitated. This can be effected by the addition to the milk of twice its volume of saturated magnesium sulphate solution and of the powdered salt until saturation is complete. The casein can then be filtered off, washed with saturated magnesium sulphate solution, and the nitrogen in it determined by the Kjeldahl process. The percentage of nitrogen found multiplied by 6·38 gives the percentage of casein. The albumin can then be found by difference, for the amount of the other proteid of milk, the globulin, is so small that it may be neglected.*

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* Sebelien, Zeits. für Physiol. Chemie. 13, 137 and 160.

Another method of precipitation of casein is the following*:—

Ten grammes of the milk, which must not be curdled, are diluted to 100 c.c. with water and raised to 40°. The casein is then precipitated by adding 1·5 c.c. of a 10% solution of acetic acid. The whole is well stirred, allowed to stand for a short time, and the precipitated casein washed three or four times with cold water. The nitrogen in the precipitate is then determined as before.

Determination of Milk Sugar.—This can be done either by the well-known Fehling method or by the use of the polarimeter. In either case previous removal of the fat and proteids from the milk is necessary. If the Fehling method is to be employed, this can readily be done by the method used by van Slyke above described, but in addition boiling the solution and filtering. For polarimetric examination an acid solution of mercuric nitrate may be employed to precipitate the proteids.† It is prepared by dissolving mercury in twice its weight of strong nitric acid and diluting the solution with an equal volume of water. It will serve to clarify fifty times its volume of milk.

Many methods of conducting the determination of lactose are in use. For details a manual on quantitative analysis should be consulted. One method of performing the Fehling test may be briefly described here.

Fehling's solution is best prepared when required by mixing equal volumes of the following solutions :—

(1) A solution of 34·64 grammes of pure crystallized copper sulphate in 500 c.c. of water.

(2) A solution of 173 grammes of sodium potassium tartrate ("Rochelle salt") and 51 grammes of sodium hydrate in 500 c.c. of water.

The filtrate from the precipitated proteids is so diluted that it occupies exactly 10 times the volume of the milk taken. 50 c.c. of this filtrate are then taken, heated in a water bath, and mixed with a previously boiled mixture of 30 c.c. of the above copper sulphate solution, 30 c.c. of the alkaline tartrate solution, and about 120 c.c. of water. The mixture is kept on the water bath for 15 minutes and filtered through a small filter paper or a Gooch's crucible. The precipitated cuprous oxide is thoroughly washed with boiling water, next with alcohol, and finally with ether. The precipitate is then dried, transferred to a weighed porcelain crucible, and strongly ignited with free access of air, so as to oxidise it completely to cupric oxide. The amount of hydrated milk sugar corresponding to the weight of the cupric oxide is then ascertained, best by reference to a table, or approximately, by multiplying the weight of the precipitate by 0·6024.

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* Van Slyke, Jour. American Chem. Soc. 15, 644.
† Wiley, American Chemical Journal, 6, 289.

Adulteration of Milk.—The commonest adulterant is water. Direct proof of the presence, in a sample of milk, of added water is very difficult unless the water happens to contain some substance not naturally present in milk, *e.g.*, nitrates. In such cases the detection of nitrates in the milk, say by the reaction with diphenylamine and sulphuric acid, becomes at once proof of the addition of water, though in some cases this may be due to the small quantities employed in rinsing out the milk cans, &c. The usual way of estimating the amount of added water is from a determination of the amount of solids not fat. By assuming that this, in genuine milk, never falls below 8·5 %, the percentage of added water is given by the expression—

$$100 - \frac{S \times 100}{8{\cdot}5},$$

in which S = percentage of solids not fat. This gives the *probable* minimum amount of added water.

Another method of calculating the probable percentage of added water is based on the assumed constancy of the sum of the "lactometer degrees" (*i.e.*, sp. gr. × 1000 − 1000) and the percentage of fat. This sum is generally about 36 and rarely falls below 34·5. Accepting this latter value as the minimum in genuine milk, the percentage of added water is then given by the expression—

$$100 - \frac{G + F \times 100}{34{\cdot}5},$$

where G = "lactometer degrees" and F = percentage of fat.*

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* Richmond, Dairy Chemistry.

Another way in which milk is impoverished is by the removal of a portion of the fat, or, what comes to the same thing, the admixture of skimmed or separated milk. The amount of fat removed can obviously only be calculated if the amount originally present in the milk be known. The usual plan is to assume that genuine milk contains 3% fat, when the percentage of the total fat removed is given by—

$$100 - \frac{F \times 100}{3}.$$

It is evident from the above figures that the calculation of the amount of added water or proportion of fat removed from a sample of milk is based upon pure assumptions as to the real character of the original milk. When the enormous variability shown by genuine milk is taken into account it will be seen how unreliable are the results of such calculations. The most that can be said of the results so obtained is that they probably express the lower limits of the alleged sophistication.

Detection of the Presence of Preservatives.

1. *Boric acid* or *borax.*—Easily detected in the ash of the milk (best obtained by igniting the residue left on evaporating the milk with lime water) by the well-known cherry-red colour which is shown by turmeric paper when dipped into a dilute hydrochloric acid solution of the ash and dried at 100°. As a confirmatory test the reddened paper should be moistened with very dilute caustic soda solution, when a blue-black colour will be produced.

2. *Salicylic acid.*—About 50 c.c. of the milk are mixed with an acid solution of mercuric nitrate and the coagulated proteids and fat filtered off. The filtrate is then shaken with ether or (better) a mixture of ether and petroleum spirit, in which the salicylic acid dissolves. The ethereal solution is then evaporated and a drop of neutral ferric chloride solution added to the residue; a violet colouration then indicates the presence of salicylic acid.

3. *Benzoic acid.*—The milk is made alkaline with lime water and evaporated with calcium sulphate or pumice to dryness on the water bath. The residue is then powdered, moistened

with dilute sulphuric acid, and extracted with dilute alcohol. The alcoholic solution is neutralised with lime water and evaporated to small volume; the residue is then slightly acidified with dilute sulphuric acid and extracted with ether. The ethereal solution is then evaporated, when the benzoic acid is left and can be recognised by its odour.

4. *Formaldehyde* in the form of "Formalin," which is a 40% solution in water of the real formaldehyde, $O=CH_2$, is a very efficient preservative. It can be detected by Hehner's test, which consists in diluting the milk with an equal volume of water, placing the mixture in a test tube, and pouring in a little sulphuric acid (specific gravity about 1·825) to which a drop of ferric chloride or other oxidising agent has been added, down the sides of the tube, so as to form a layer at the bottom. If formaldehyde be present a violet or blue colour occurs at the point of contact of the two layers. In this reaction Hehner* finds that the casein of the milk takes part; it cannot, therefore, be obtained with aqueous solutions of formaldehyde.

5. *Fluorides* or *Fluosilicates* are also possessed of good antiseptic properties. They can be detected, if present, in the ash of the milk by the usual reaction for hydrofluoric acid—its etching effect on glass when it is liberated by the action of strong sulphuric acid.

BUTTER.—With genuine butter, the chief differences in chemical composition are in the proportions of water, salt, and casein. These are determined by drying a weighed quantity in a flat-bottomed dish at 100° until it ceases to lose weight; the loss gives the water present. The residue is then extracted repeatedly with ether, the insoluble matter dried and weighed. The weight gives the amount of casein and salt. The residue is then treated with hot water, filtered, and the amount of chlorine determined by titration with standard silver nitrate, using potassium chromate as indicator, in the usual way.

The most difficult part of such analytical processes is the taking of a satisfactory sample; the amount of water present usually varies very much in different parts of the same mass of butter. Probably the best way is to melt a considerable quantity of the butter at as low a temperature as possible in a stoppered bottle and shake it continually until it stiffens.

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* Analyst 1896, 92; J.C.S. 1896, abst. ii. 583.

If the butter is to be tested for possible adulteration with other animal fats, "oleomargarine," &c., the procedure is more complicated. As already explained, butter fat differs from other natural glycerides in containing considerable quantities of fatty acid radicals of low molecular weight, *e.g.*, butyric acid. Butyric acid and its neighbouring homologues are soluble in water and volatile in steam, while the higher fatty acids are both insoluble and non-volatile. Upon these facts most of the methods of analysis are based.

The method adopted (though numerous modifications in detail have been introduced) is essentially the decomposition of a known weight (generally 5 grammes) of butter with excess of caustic soda, whereby glycerol and soaps are produced. The latter are then decomposed with a slight excess of dilute sulphuric acid, thus liberating the fatty acids. The liquid is then distilled until a certain proportion of it has passed over, and the acidity of the distillate is then determined by means of decinormal soda or baryta solution and phenolphthalein.

Aqueous soda saponifies butter very slowly and is now rarely or never used. An alcoholic solution works much more rapidly and the alcohol is readily expelled by heat before the soap is decomposed by sulphuric acid. A solution of caustic soda in glycerol saponifies the butter very quickly, especially as it can be raised to a high temperature, and the presence of the glycerol does not interfere with subsequent operations. This modification of the original Reichert process, as it is called, was introduced by Leffmann and Beam. The following reagents are used:—

Soda solution.—20 grammes of pure caustic soda are dissolved in 20 c.c. of water; 20 c.c. of the clear solution are then mixed with 180 c.c. of pure glycerol.

Sulphuric acid.—1 volume of pure acid to 4 volumes of water.

Barium hydrate.—A decinormal solution.

The sample is melted and filtered from casein, &c. 5 grammes (about 5·75 c.c.) of the melted fat are then run into a 300 c.c. flask, previously thoroughly dried and weighed.

After cooling, the flask and fat are weighed. 20 c.c. of the glycerol solution of soda are then run in and the flask heated directly over the lamp. After the water (in the soda solution) has boiled off, the contents of the flask will become quite clear in a few minutes. The flask, now containing glycerol and soap, is allowed to cool and 135 c.c. of water added. When the soap is dissolved, 5 c.c. of the sulphuric acid and a piece of pumice are added, the flask connected to a glass condenser fitted with a bulb arrangement to prevent spirting, and 110 c.c. are distilled over in half an hour. The distillate, which must be filtered if not clear, is then titrated with the alkali after addition of a few drops of phenolphthalein. 5 grammes of butter treated in this way require from 24 to 34 c.c. of decinormal alkali, while 5 grammes of most animal fats require less than 1 c.c.

Commercial "margarine," which consists of animal fats churned with milk so as to acquire a flavour of butter, usually requires from 1 to 2 c.c. of decinormal alkali.

Another method of distinguishing butter fat from other fats is by determining the amount of alkali necessary for saponification of a fixed quantity of the fat, or what is practically its reciprocal, the "saponification equivalent," *i.e.*, the weight of fat equivalent to the gramme equivalent of the alkali. The saponification equivalent of butter, in consequence of the acids of low molecular weight which it contains, is much smaller than that of most other fats, the actual values found being about 247 for genuine butter and about 288 for most other fats. For other methods the reader must refer to some manual of analysis.

Butter Colouring.—The natural colouring matter of milk is apparently contained in the fat and is subject to considerable variation. The amount is usually least in winter, and at that season butter is often white in colour. It is a common practice to add some colouring substance to the cream in the churn, so that the colour of the butter may be deeper. The usual addition is *annatto*, a colouring matter obtained from the seeds of *Bixa orellana.*

The colouring substance is soluble in alkaline solutions and in oils. The commercial solution generally contains sodium carbonate. Other colouring matters, *e.g.*, carrot juice, turmeric, saffron, marigold, and even chrome yellow (lead chromate) have been occasionally used. The last mentioned is highly objectionable and poisonous. Its presence would be indicated by the occurrence of lead and chromium in the ash. Annatto can be detected by taking about 5 grammes of butter, dissolving it in about 50 c.c. of ether, and then shaking vigorously with about 15 c.c. of very dilute caustic soda. The whole is set aside, when it separates into two layers, the upper one consisting of an ethereal solution of fat, the lower containing the annatto, if present. Some of the lower liquid is then removed, evaporated to dryness, and the yellow residue treated with a drop of strong sulphuric acid. If annatto be present a blue or violet colour is produced, quickly changing to green, and finally to a brownish hue. Another way of separating artificial colouring matter from butter is due to Martin. A mixture of about 2 parts of carbon disulphide and 15 of alcohol is made, and 5 grammes of butter are treated with 25 c.c. of this liquid and the whole well shaken. On standing, the carbon disulphide, with the fat, sinks to the bottom, and the colouring substances remain in the alcohol.

CHEESE.—In cheese the usual constituents determined in an analysis are water, ash, fat, and casein, and although the last mentioned is the characteristic ingredient, the value of a sample depends far more upon the amount of fat which it contains than upon its casein content.

Water is determined by heating about 5 grammes of the sample, in thin slices, in a weighed dish containing some asbestos, which serves to absorb the melted fat. The heating should be done in a steam oven and extend over at least 10 or 12 hours. The loss in weight gives the water.

Ash.—The residue from the previous determination is set on fire, when the asbestos will act as a wick, from which the fat will burn. The dish is then heated to low redness until the black carbon particles disappear.

Fat.—About 5 grammes of the cheese are rubbed up in a mortar with about 10 grammes of anhydrous copper sulphate. The mixture is introduced into a Schleicher & Schüll's filter-paper thimble and extracted with ether for eight or ten hours in a Soxhlet extractor. The ether is then distilled off and the fat weighed.

Casein.—The total nitrogen is determined by the Kjeldahl process,* using about 2 grammes of cheese. The percentage of nitrogen is then multiplied by 6·38 and the product taken as casein.

These methods are those usually employed, but are not entirely satisfactory. Attempts to differentiate between the products of ripening have been made,† but they are too complicated to be discussed here.

MILK STANDARDS.—The establishment of a standard by which to judge of the quality and freedom or otherwise from adulteration of a sample of milk has received much attention and consideration. A few months ago (September, 1901) the Board of Agriculture decided to take 3% of fat and 8·5% of solids not fat, as the probable lower limit in the case of genuine milk, and it was enacted by law that if a specimen did not come up to these figures a presumption should be raised that it was not genuine, by reason of the abstraction of fat or the addition of water. While these values are much below the average, and to that extent satisfactory from the producers' point of view, it must be remembered that with morning milk, when the night interval is much longer than the day one, the fat content of genuine milk may often be below this standard. Indeed, according to the experience of the author during the very dry autumn of 1901, the mixed milk of dairy shorthorn cows in the morning, was far more often below than up to this standard. The cows were at pasture, but received 2℔. decorticated cotton cake each per day. For evening milk, on the other hand, the standard for fat is very much below the average, and lower, perhaps, than the consumer has the right to expect.

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* v. p. 94. † v. Chap. XIV.

The difficulty of choosing a satisfactory standard is great, and perhaps almost insuperable, when the great differences which are often shown between evening's and morning's milk are taken into account. If cows could be milked at regular intervals of twelve hours each, these differences would be greatly diminished, but unfortunately the exigencies of the trade almost necessitate great inequalities in the intervals between milkings. A different standard for morning and for evening milk would, perhaps, better meet the case; but, in practice, difficulties in administering the law would arise.

It is, however, highly desirable that an authoritative statement should be made as to the exact meaning of the new Regulation. Whether it is to be understood that all milk sold to the public must contain at least 3 % fat and 8·5 % solids not fat, or whether, so long as the sample can be proved to be the genuine product of the animals, the existence of lower values for fat and solids is not sufficient to ensure conviction, seems at present to be uncertain.*

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* From a circular, issued by the Board of Agriculture on Dec. 28th, 1901, it appears probable that the latter interpretation is desired, but that if the fat in milk be found to be below 3%, the onus of proving the genuineness of the sample then falls upon the purveyor.

CHAPTER XVI.

MISCELLANEOUS PRODUCTS USED IN AGRICULTURE.

IN this chapter, which is necessarily disconnected and fragmentary, such substances as find applications in agriculture are briefly described from their chemical aspect, while some reference is made, in most cases, to the manner and proportion in which they are used. An alphabetical arrangement has been adopted, since the matters to be dealt with are so numerous and diverse that any connected or continuous description would be impossible. In some cases the substances mentioned have already received notice in the preceding chapters; when this is the case, reference to the place is given, so as to avoid unnecessary repetition.

Arsenious Oxide, As_4O_6 (in the state of vapour). This substance is known in three distinct forms, viz., one *amorphous* or *vitreous* and two *crystalline*—regular octahedra and trimetric prisms. Ordinary *white arsenic* consists mainly of the powdered vitreous variety, which, however, tends to pass into the heavier, octahedral form. The specific gravities of the vitreous and octahedral varieties are about 3·7 and 4·0 respectively. Their solubilities in water vary with circumstances. If water be shaken for a long time at 15° with the solids the amounts dissolved by 100 parts of water are 0·28 of the crystalline and 0·92 of the vitreous varieties, while if saturated solutions at 100° be cooled to 15°, 2·18 of the crystalline and 3·33 of the vitreous form remain in solution.

Arsenious oxide dissolves readily in solutions of caustic alkalies or of alkaline carbonates, arsenites of the alkali metals being formed. "Fowler's solution" contains potassium arsenite. Arsenious acid, as the oxide is often called, and its compounds, are powerful poisons both to animals and plants, but curiously have much less influence upon micro-organisms. Indeed certain moulds can develop in the presence of considerable quantities of arsenic and evolve arsenuretted hydrogen. Thus one of the most delicate tests for the presence of arsenic (Abba's test) consists of introducing into the suspected substance a strong culture of *Penicillium brevicaule* and observing the garlic-like odour evolved. As little as $\frac{1}{500}$ of a milligramme can thus be detected.*

In culture solution as little as 0·0002% of arsenious acid will destroy plants.† Arsenic acid and arsenates (compounds of As_2O_5) are much less injurious, for plants will grow in solutions containing as much as 0·02%‡.

Arsenious oxide is sometimes used in medicine as a nerve tonic, and by repeated small doses a person may acquire the power of taking, without danger, quantities which far exceed the normal lethal doses. In such cases, however, ill effects upon the system are generally produced by continual dosing with arsenic. The administration of arsenic in small quantities often produces a plumpness and sleekness of the skin. For this reason it is often secretly given to horses by farm servants, often with fatal results. Considerable publicity has lately been given to the prevalence of this practice in the north of Yorkshire, and many cases of serious losses of horses have occurred from this cause.

Arsenious oxide finds a more legitimate use in sheep dips, especially for foot-rot and as a vermin poison.

Bleaching Powder—Chloride of Lime, Ca(OCl)Cl, is used chiefly as a disinfectant. It acts by evolving hypochlorous acid, HClO, which is a strong oxidising agent and thus able to destroy putrescible matter and micro-organisms. The hypochlorous acid is set free by the carbon dioxide of the air, thus:—

$$2CaCl(OCl) + CO_2 + H_2O = 2HClO + CaCl_2 + CaCO_3.$$

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* Scholtz, Jour. Chem. Soc. 1900, abst. ii. 244; also Abel and Buttenberg, Jour. Chem Soc. 1900 abst. ii. 299.

† Arsenic is often found in sulphuric acid and therefore in sulphate of ammonia and in superphosphate. Usually, however, care is taken to employ acid free from more than traces of arsenic in the preparation of these substances. According to Haselhoff (Jahresbericht ü. Agricultur-Chemie 1900, 126) superphosphate made with sulphuric acid from German pyrites contains about 0·05% of arsenic; with acid from Spanish pyrites, as much as 0·149% of arsenic. He concludes that little danger exists of the arsenic in superphosphate being sufficient to do harm.

‡ Stoklasa, Ann. Agron. 1897, 471; J.C.S. 1898, abst. ii. 131.

A more rapid and more powerful effect is produced if the bleaching powder be treated with dilute acids, when chlorine is evolved, thus:—

$$CaCl(OCl) + H_2SO_4 = CaSO_4 + H_2O + Cl_2.$$

The chlorine acts as a most effective disinfectant. It very rapidly destroys micro-organisms, even when much diluted with air, but is, like all disinfectants, less successful with their spores. According to Fischer and Proskauer, to be effective, about 0·5 % of chlorine by volume should be present in the air. This would require the consumption of about 2lb. or 3lb. of bleaching powder per 1000 cubic feet of air space. Usually, however, about half this quantity is employed.

Chlorine fumigation has been successfully used for disinfection after swine fever[*] and plague.[†]

Other hypochlorites have been used, and a process known as the "Hermite" process, by which sea-water is electrolysed and the fluid so obtained used for disinfecting sewage, &c., depends for its action upon the production during electrolysis of hypochlorites, probably chiefly of magnesium.[‡]

Copper Salts.—*Soluble* copper salts are extremely poisonous to plants. In water cultures it was found that the presence of 0·0055 part of copper sulphate in 100 parts of water was sufficient to kill young wheat plants; while 0·0049 of the bromide, 0·0050 of the chloride, or 0·0061 of the nitrate produced a similar effect.[§] On the other hand, *insoluble* copper compounds not only appear to be non-poisonous but are often taken up by the plant. Haricot beans grew even better in nutrient solutions to which copper oxide had been added.[||] Copper is said to be often present in plants to the extent of 0·003 %, even on ordinary soils, while as much as 0·056 % may be present in the dry matter of plants growing on soils containing much copper.[¶] In Australia a plant—*Polycarpæa*

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[*] Klein.

[†] Crow and Browne, 1894

[‡] See Roscoe and Lunt, J.S.C.I. 1895, 224.

[§] Coupin, Comt. Rend. 1898, 400; J.C.S. 1899 abst. ii. 118.

[||] Tschirch, Ann. Agron. 1895, 544; J.C.S. 1896 abst. ii. 328.

[¶] MacDougal, Exper. Stat. Record 1899, 24; J.C.S. 1900, abst. ii. 235.

spirostylis—has been found to contain as much as 0·05% of copper, and its presence in any district is regarded as an indication of copper in the soil.* Large quantities of copper salts, however, especially if they be present as sulphide, in which case, by oxidation, soluble sulphate is probably slowly formed, appear to be injurious. The author found, in a soil in which fruit trees refused to grow, about 0·2% of copper oxide, probably derived from pyrites.

Copper salts find their chief use in agriculture as fungicides. The most important commercial salt is the sulphate, occurring crystallized as "blue vitriol," $CuSO_4.5H_2O$. This substance—which was formerly often adulterated, especially for agricultural purposes, with the much cheaper ferrous sulphate, with which it is isomorphous—is now very largely used, and the modern product is, as a rule, fairly pure.

The pure salt has a specific gravity of 2·28 and a solubility in 100 parts of water which varies from 31·6 at 0° to 203·3 at 100°. At 10° 100 parts of water dissolve about 37 parts, at 20° about 42·3 parts of the crystallized salt.

A solution containing 2% of $CuSO_4.5H_2O$ has a specific gravity of 1·0126, a 4% solution 1·0254, and a 6% solution 1·0384. Copper sulphate is insoluble in absolute alcohol, though very slightly soluble in aqueous alcohol; it is much more soluble in glycerine.

Copper sulphate has long been used for dressing seed wheat, with a view to the prevention of such fungoid diseases as *smut*, *rust*, and *bunt*. For this purpose each quarter of corn receives 2 gallons of water in which about 2℔. of copper sulphate crystals have been dissolved. The dressing is usually applied about 24 hours before sowing and the grain is thoroughly mixed and incorporated with the solution. Each grain of wheat becomes coated with the liquid, which on evaporation leaves a thin film of the salt. The spores of the fungi are thus destroyed, but the copper is converted into insoluble compounds soon after the seed is sown and before germination of the wheat embryo commences. The corn, therefore, is not injured, though it would probably be killed outright if it were not for the action of the constituents of the soil (probably mainly the calcium carbonate) upon the copper sulphate. In America the grain is soaked in a solution of 1lb. copper sulphate in 24 gallons of water for 12 hours and then for 5 minutes in lime-water.* Dressings of copper sulphate are also now recommended for barley and oats, for preventing smut.

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* Heckel, J.C.S. 1901, abst. ii. 331.

Copper sulphate is also employed in solution for spraying plants, with the object of preventing fungoid diseases. For this purpose a solution containing about 0·5% of the salt is usually employed. Stronger solutions would be apt to injure the foliage of certain plants.

Another use of copper sulphate is in the destruction of cruciferous weeds in cereal crops, *e.g.*, charlock in barley or oats. This is effected by spraying the field—when the charlock plants are still small, best when 2 or 3 inches high, and before the stem and flower are formed—with a 2 or 3% solution of the salt, at the rate of about 40 gallons per acre. To be successful the operation should be performed in dry, sunny, calm weather. It is then found that the charlock leaves blacken and the plants die, while the barley and clover not only are not injured, but appear, in many cases, to be benefited by the process. This plan of dealing with charlock was apparently first tried in 1897 by Girard in France. He used a 5% solution and ascribes the destruction of the charlock to the poisonous effect of the solution, which would be retained on the rough and more or less horizontal leaves of the charlock, while it would quickly run off the smooth and erect leaves of the cereals. It is doubtful whether this opinion is entitled to much weight, as clover, which also has horizontal leaves, suffers little or no damage. It is possible that the action is in some way dependent upon the presence in the charlock (as in other cruciferæ) of organic sulphides or sulphocyanides, and that some reaction of the copper upon these compounds is the cause of the injury.

Another possible explanation of the toxic action of copper and iron sulphate solutions is that in contact with the cells of plants, osmotic pressure is set up owing to the liquid outside being more concentrated than that in the protoplasm of the cell. Water therefore leaves the protoplasm, and shrinkage occurs ("plasmolysis"), so that the vital processes of the plant are interfered with, perhaps by the destruction of the continuity of the protoplasm. If, through differences in the strength and thickness of the cell walls, this action takes place more readily in such plants as charlock, &c., than in cereals, this explanation would seem to be sufficient to account for the facts. It receives confirmation from the discovery, quite recently made, that spraying with 15 or 20% solutions of sodium nitrate, ammonium sulphate, or potassium chloride—salts which cannot be suspected of having any chemical toxic effects—is also effective in destroying charlock.* (See also iron sulphate.)

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* Farmers' Bulletin, No. 75, U.S. Dept. of Agric.

Copper hydroxide, $Cu(OH)_2$, is also largely employed as a fungicide for application to vines, potatoes, and fruit trees. It is usually employed in the form of "Bordeaux mixture," which is made by adding lime (best in the form of "milk of lime") to copper sulphate solution. Various strengths of solution have been recommended, the proportion of copper sulphate varying from 12lb. to 30lb. per 100 gallons of water, that of quick-lime from 8lb. to 20lb. The lime should in all cases be first slaked, made into a smooth cream with water, and then poured into the copper sulphate solution with constant stirring. For many purposes it is highly important that the lime should be in excess and the mixture therefore free from any dissolved copper compounds, since these act corrosively upon the foliage. This can readily be detected by inserting a piece of bright iron or steel, when no deposit of metallic copper should form; or another easily applied test is to breathe upon the surface of a portion of the mixture, when a film of calcium carbonate should be formed, showing the presence of free calcium hydrate. The mixture should be kept constantly stirred and be applied by the sprayer as soon after its preparation as possible.

Bordeaux mixture is largely used in the preventative treatment of vines and potatoes and is highly effective.

Other copper compounds used as fungicides are—

1. "*Eau celeste,*" which is essentially ammonio-copper sulphate, $CuSO_4.4NH_3.H_2O$, the well-known magnificent

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* Heinrich, Jahresbericht über Agricultur-Chemie, 1901, 351.

blue solution formed when ammonia is added in excess to a solution of copper sulphate. The usual proportions are about 5lb. blue vitriol and 6 or 7 pints of strong ammonia in 100 gallons of water.

2. *Ammoniacal copper carbonate*, made by dissolving copper carbonate in ammonia or ammonium carbonate solution. Quantities often used are—copper carbonate 10 ounces, strong ammonia 6 pints, water 100 gallons.
3. *Copper sulphate and sulphur powder.*—A mixture of equal weights of powdered blue vitriol and air-slaked lime is mixed with 20 times its weight of powdered sulphur.

Copper sulphate and ammonio-copper sulphate also find a limited application in veterinary practice as astringents.

Copper sulphate is also used as a disinfectant in France, a 5% solution being recommended. It has been employed as a disinfectant for cow-sheds after rinderpest, but is expensive.

Disinfectants.—A true disinfectant is a substance which destroys the organisms (and their spores) which produce putrefaction or disease. An antiseptic, on the other hand, is a substance which prevents their growth, though it may or may not destroy them. A deodoriser is a body which absorbs or destroys the evil-smelling gases which are evolved during processes of decay.

Disinfectants act in various ways and it is impossible to exactly correlate their germicidal action with their chemical or physical properties.

Rideal* classifies their action thus:—

1. Free acids or salts of acid reaction retard the growth of most bacteria.
2. Albumen is precipitated by soluble salts of many heavy metals, *e.g.*, mercury, copper, &c. Such salts probably act by coagulating the protoplasm in the organisms.
3. By combining with such metals, or in other ways, *e.g.*, by contact with charcoal, the food of bacteria may be rendered insoluble and the organisms are thus starved.

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* Disinfection and Disinfectants, 1895, 145.

4. Reducing agents, *e.g.*, sulphites, ferrous salts, &c., remove oxygen and so destroy aerobic organisms.
5. Oxidising agents, *e.g.*, chlorine, ozone, hydrogen peroxide, permanganates, &c., destroy by oxidation both the bacteria and their food. These are the most perfect disinfectants.
6. Some easily reducible metallic salts are assimilated by the bacteria with the deposition of the elements within their tissues. This deposition when it becomes great enough kills the organisms. This happens with salts of gold and silver. In some cases very minute quantities of these poisons promote the growth of the same organisms, which larger doses quickly destroy.
7. Some substances which are germicides act in a manner which can only be described as physiological and not chemical. To this class belong boric acid and the borates and many of the aromatic compounds.

The number of substances which have been used as disinfectants is very great and is constantly being increased.

Among many others, the following may be mentioned:—

Chlorine, both as the free element, as hypochlorous acid, and as hydrochloric acid.

Bromine and iodine.—The former has some advantages because of its being liquid and is now sufficiently cheap to permit of its use; the latter is less convenient and too costly for general purposes. They act, like chlorine, best in the presence of moisture. Iodine trichloride, ICl_3, has also been highly recommended.

Hydrofluoric acid, HF, and especially hydrofluosilicic acid, H_2SiF_6, and the silicofluorides, are highly antiseptic.

"Salufer" is a patented disinfectant, the basis of which is silicofluoride of sodium, Na_2SiF_6. The use of hydrofluosilicic acid as a preventative of the decay of farm-yard manure has already been alluded to. Fluorides are also employed to prevent undesirable fermentations in breweries.

Oxygen is the best natural disinfectant, and free admission of oxygen destroys many micro-organisms. It is by absorption of atmospheric oxygen that river water polluted by putrefying organic matter purifies itself. Unfortunately the process is slow.

Ozone, O_3, the allotropic form of oxygen, is much more powerful in its action, and attempts to apply it as a disinfectant have been made. The cost of its production by the silent electrical discharge, and the fact that only about 2 % of the air can be converted into ozone, render the success of these attempts doubtful, especially as ozone would probably first attack the oxidisable organic matter before the micro-organisms.

Hydrogen peroxide, H_2O_2, is an excellent disinfectant, and though a powerful germicide has no influence upon enzymes, *e.g.*, those of digestion.

When air is brought into contact with oil of turpentine in the presence of water, hydrogen peroxide is formed. Advantage is taken of this in the preparation of "Sanitas," a preparation made from terpenes and possessing a characteristic odour.

Sulphur dioxide, SO_2.—This gas, of well-known properties, is a powerful disinfectant and deodoriser. It is poisonous and very irritant when breathed, 5 % in air producing fatal results.

It dissolves in about $\frac{1}{50}$ of its volume of water, yielding a weak solution of the unstable sulphurous acid, H_2SO_3.

It acts in presence of water as an acid, and therefore unites with ammonia, amines, organic bases, &c. It decomposes sulphuretted hydrogen or ammonium sulphide and reduces many organic substances, generally producing colourless compounds. Hence its use in bleaching wool, &c.

By pressure it can be condensed to a liquid and is now commercially obtainable in glass siphons (under a pressure of about three atmospheres), each of which will yield about 500 litres of the gas.

The usual plan of generating the gas is by burning sulphur in air. The sulphur is either in the form of "candles," *i.e.*, cylinders provided with a wick, or a cheaper method is to use roll sulphur placed in metal dishes and moistened, when everything is ready, with the very inflammable and volatile carbon disulphide; the ready ignition of the sulphur can thus be ensured. According to the Local Government Board's direction, 1½lb. of sulphur should be used for an ordinary room; this probably would yield air containing about 2 % of SO_2.

In Belgium from 20 to 30 grammes per cubic metre are recommended (*i.e.*, from 2 to 3 %).* Considerable difference of opinion appears to exist as to the value of sulphur dioxide as a disinfectant.

Carbon disulphide, CS_2, the very volatile, inflammable liquid, with the well-known offensive odour, is poisonous both to animals and micro-organisms. Its proposed use as a means of checking nitrification in soils in the autumn has already been alluded to. On combustion it yields carbon dioxide and sulphur dioxide. With alkaline sulphides it forms thiocarbonates or xanthates (*e.g.*, K_2CS_3), which are sometimes used in treating plant diseases.

Manganate and permanganate of soda or potash, K_2MnO_4 and $KMnO_4$.

These are powerful oxidising agents, but being non-volatile require to be brought into actual contact with the substance to be oxidised. All oxidisable matter, *e.g.*, nitrites, ferrous salts, organic matter, is first attacked, before the micro-organisms are affected.

These substances form the active ingredients in "Condy's fluid."

Zinc chloride, $ZnCl_2$, a deliquescent and caustic white solid, very soluble in water.

It is a powerful disinfectant. A solution containing about 50 % of zinc chloride constitutes "Burnett's disinfecting fluid." A more dilute solution is often used in surgery as an antiseptic.

Carbolic acid, phenol, C_6H_5OH, and its homologues, *e.g.*, *cresol*, $C_6H_4(CH_3).OH$, have long been used as antiseptics and disinfectants.

They are obtained from coal-tar or from the tar produced by the distillation of wood.

These substances are poisonous in large quantities and when undiluted are caustic and generally deliquescent. They are only slightly soluble in water, but by the action of alkalies they yield salt-like bodies—"carbolates" or "phenates"—which are readily soluble and easily decomposed by acids, even by carbonic acid, yielding again the free phenol.

Many disinfectants consist of lime or magnesia containing about 15% of phenol. Such powders gradually lose their phenol on exposure to air. Pure phenol is a colourless crystalline body, melting at 41° and boiling at 182°. With a little water it liquefies, forming a fluid hydrate, which, however, is only soluble in about 15 times its weight of water.

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* Rideal, Disinfection and Disinfectants.

Phenol is decidedly antiseptic, but recently doubts have been expressed as to its disinfectant powers. Certain pathogenic organisms are very resistant to phenol, *e.g.*, the typhoid bacillus can be separated from many other micro-organisms by taking advantage of its power of growing in carbolised nutrients.*

Phenol is a violent plant poison, and a very dilute solution will prevent the germination of seeds. It is sometimes used as a weed destroyer.

Many of the "disinfecting powders" of commerce consist essentially of an indifferent powder, *e.g.*, silicates or even silica, containing about 15% of carbolic acid. They are often coloured pink. Sometimes calcium sulphite is also present.

Creasote or *creosote* is a mixture of cresol, $C_6H_4(CH_3)OH$, xylenol, $C_6H_3(CH_3)_2OH$, and other higher members of the series; about 1 or 2% of phenol is usually present. It is colourless when fresh, but soon darkens. It possesses good antiseptic powers and is thought to be preferable to phenol. It is used in the preservation of timber.

Many preparations containing cresols are in use as disinfectants. *Lysol* is obtained by mixing tar-oils (chiefly cresol) with fat and saponifying with potash. It is soluble in water and is apparently an excellent antiseptic.

Jeyes' disinfectant and *creolin* also contain alkalies and cresols.

Izal is a reddish brown liquid, slightly heavier than water, obtained in the process of coke manufacture in closed ovens. It has antiseptic properties and, in strengths of 1 in 200, is a good disinfectant. It has also been used with success as a constituent of sheep dips. It has the advantage of being non-volatile and therefore remains on the wool for a long time.

Wood creasote is a more powerful disinfectant than that from coal tar. In addition to cresol and phenol it contains *guaiacol*,

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* Rideal, Disinfection and Disinfectants, p. 151.

$C_6H_4(OCH_3)OH$, and *creosol*, $C_6H_3(CH_3)(OCH_3).OH$. Wood creasote is very poisonous both to animals and plants.

"Little's soluble phenyle" is said to be obtained from wood creasote.*

Many other antiseptic and disinfectant substances have been obtained from coal tar. For an account of these substances a treatise on organic chemistry should be consulted.

"*Formalin*," the commercial name for a solution of formaldehyde, H_2CO, in water. The nominal strength is 40% of formaldehyde and a trace of formic acid is also present. The liquid is stable in closed vessels, but loses the gas on free exposure to air.

Formaldehyde is one of the most powerful antiseptics and disinfectants. Solutions of 1 in 10,000 or 20,000 will prevent the growth of many micro-organisms and 1% solutions produce absolute sterility.

Formaldehyde is an admirable fungicide and in sufficient quantities acts as a powerful plant poison.

In 1897 Windisch† investigated the effect of various strengths of formaldehyde solutions upon the germination of cereals. In each case 200 seeds were allowed to germinate between thick filter paper moistened with water and with 0·02, 0·04, 0·08, 0·12, 0·20, and 0·40% formaldehyde solutions.

Wheat was almost wholly destroyed by the 0·12% solution, whilst oats were only delayed in their germination by this solution; with 0·20% solutions, barley, wheat and rye were destroyed, and with 0·40% solutions, oats also succumbed. In 1901 he‡ extended the experiments to other seeds; the 0·2% solution killed flax and rape and greatly injured lupins, peas, and clover, retarded the germination of horse-beans, but did not injure maize. Even a 0·4% solution, which killed all other seeds, did not destroy maize.

By shorter treatment of seeds with formaldehyde, it has been attempted to destroy the smut spores in grain without injuring the seed. Kinzel§ found that a 0·1% solution of formaldehyde applied for one hour to rye, wheat, oats, barley, clover, and lupins had no injurious effect upon the seed, but destroyed, almost completely, the spores of fungi.

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* Rideal, p. 176. † Landw. Versuchs.-Stat. 1897, 223; J.C.S. 1898, abst. ii. 40.
‡ Landw. Versuchs.-Stat. 1901, 241; J.C.S. 1901, abst. ii. 466.
§ Landw. Versuchs.-Stat. 1898, 461; J.C.S. 1898, abst. ii. 302.

"Formalin" has been used as a preservative for food stuffs, milk, butter, &c.; but since it combines with proteids and also has an inhibitive effect upon enzymes, its use for this purpose is not to be recommended.

Fungicides.—These are in nearly all cases plant poisons, but are used under such conditions or in such dilute solution that they do not injure the higher plants. Some of the more important fungicides are—

Copper salts, *v.* p. 365.

Ferrous sulphate, *v.* p. 378.

Mercuric chloride.—This has been recommended and used in America as a remedy for bunt or stinking smut in wheat. The seed is treated with a 0·2% solution, conveniently made by dissolving 1℔. of corrosive sublimate in 50 gallons of water.

Formaldehyde, *v.* p. 374.—For prevention of bunt in wheat or smut in oats a solution of 1℔. "formalin" in 50 or 60 gallons of water is recommended. The seed is to be soaked for two hours in this solution, which would contain about 0·08% of formaldehyde.

Potassium sulphide.—The substance used is generally "liver of sulphur," a dark brown fused mass of sulphide and various polysulphides of potassium. An American recipe for smut in oats is to soak the grain for 24 hours in a 0·6% solution (*i.e.*, 1½℔. of potassium sulphide in 25 gallons of water) or for two hours in a 2% solution.

Hot water.—It is possible, in the case of many seeds, to kill the spores of fungi by means of hot water, without injuring the seeds themselves. This is done by dipping them into water at a temperature of about 56° and taking care that every grain is wetted. Ten minutes' treatment is found to suffice for destroying bunt in wheat or smut in oats. If the grain be soaked for three or four hours in cold water first, five minutes in the hot water is sufficient. For smut in barley the temperature should not be higher than 54·5°.

It is said that when grain is treated with hot water or with potassium sulphide there is an increase in the yield greater than would be produced if every infected grain were replaced by a sound one.*

Sulphur.—Used in fine powder for certain forms of mildew; occasionally as vapour (not sulphur dioxide), by heating sulphur to the boiling point and carefully avoiding inflammation. It can only be used in this way in enclosed spaces, *e.g.*, greenhouses. A mixture of finely-divided sulphur and lime is also employed as a remedy for mildew.

Insecticides.—In the choice of a substance to be used for the destruction of insect pests, it is necessary to consider whether the particular insects are gnawing insects, *i.e.*, whether they actually bite away portions of the plant, or sucking insects, which derive their nourishment by imbibing the sap or juice of the plant.

If the former, any violent poison which does not harm the plant may be distributed over the leaves or stems and may be effective; in the latter the substance must act upon the insect in some other way than as a poison, either corrosively upon its body or through its breathing apparatus.

As Food Poisons arsenical compounds are mainly used, the favourite ones being *Paris green*, copper aceto-arsenite [$Cu(C_2H_3O_2)_2.3Cu(AsO_2)_2$ (?)]; *London purple*, chiefly calcium arsenite and waste colouring matter; and to a less extent *Scheele's green* ($CuHAsO_3$), and *lead arsenate*, made when required by mixing solutions of sodium arsenate and lead acetate. Free arsenious oxide is not suitable for the purpose, on account of its corrosive effect upon foliage. According to American experiments† the arsenical preparations are less likely to injure the plant the less soluble the arsenic is, the order of solubility being given thus, beginning with the least soluble—lead arsenate, Scheele's green, Paris green, London purple. They are best applied in suspension in water as a spray; but sometimes they are used in the dry state, either alone or mixed with flour. In some cases they are employed as poisoned bait, mixed with sugar and bran. For spraying, about 1 part of the solid suspended in from 1000 to 2000 parts of water is generally employed. The addition of lime is said to prevent the corrosive action of arsenic compounds upon foliage.

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* Swingle, Farmers' Bulletin 75, U.S. Dept. of Agriculture.

† Marlatt, Farmers' Bulletin No. 127, U.S. Dept. of Agriculture.

For sucking insects, **contact poisons** as distinguished from food poisons have to be used. *Soap* of any kind, but particularly potash or soft soaps, in from 5 to 20 times its weight of water, is effective on the small scale. *Pyrethrum*, the ground flowers of the plant of that name, is also effective.

Flowers of sulphur, too, is useful for the purpose, as is also a solution of calcium or sodium sulphide, made by boiling sulphur with lime and water or with a solution of caustic soda.

Petroleum, either alone or, better, in most cases, as an emulsion with soap and water or with sour milk, is highly recommended. The proportions used are 2 gallons of petroleum to 1 gallon of water containing half a pound of (preferably) whale-oil soap, or to 1 gallon of sour milk. The emulsion is made by means of a force-pump. For use the emulsion is diluted with 15 or 20 times its volume of water and applied with a sprayer.

Fumigation.—Tobacco smoke is often used in green-houses as a means of destroying insect pests. For shrubs and trees extensive use is now being made in America of *hydrocyanic acid*. The tree or shrub is enclosed in a tent made of canvas rendered gas-tight by treatment with boiled linseed oil, and the gas is evolved by the action of dilute sulphuric acid upon potassium cyanide. From 30 to 40 minutes' treatment is all that is necessary, and the quantity of pure cyanide to be used appears to be about 1 to 1½ ounces per 100 cubic feet of enclosed space. The cyanide should be dropped into a glass or earthenware jar containing about three times its weight of water and its own weight of commercial sulphuric acid. It is hardly necessary to say that the greatest care has to be taken to avoid breathing air containing any hydrocyanic acid. Plants are not readily injured by the gas in the dark, but when in leaf are quickly killed by it in sunlight.

Carbon disulphide, CS_2, is an effective poison for most insects. It is used for low-growing plants which can be surrounded by boxes to enclose the heavy vapour given off from a small quantity (5 or 10 c.c.) of the liquid placed in a saucer. It is, however, particularly well adapted for the destruction of subterranean insects or their larvæ. For this purpose a hole from 6 to 12 inches deep is made, not too near the tree whose root is affected by the insects, and from 15 to 30 c.c. of carbon disulphide poured in. The hole is then quickly closed, when the vapour diffuses into the soil and destroys the insects. Carbon disulphide is also employed to rid grain of insects.

The extreme inflammability of its vapour renders carbon disulphide dangerous to use in the neighbourhood of flames.

Iron Sulphate, $FeSO_4.7H_2O$, *copperas, green vitriol.*—This substance is prepared by the action of dilute sulphuric acid upon scrap iron; sometimes by the oxidation, by means of damp air, of marcasite or white pyrites, FeS_2; or as a bye-product in the manufacture of alum from "alum schists," *i.e.*, shales containing iron pyrites.

It forms monoclinic crystals of light green colour, which effloresce and oxidise when exposed to dry air, a yellowish powder consisting of ferric hydrate and ferric sulphate being produced. 100 parts of water dissolve—

60·9	parts	of the	crystallized salt at	10°
70	,,	,,	,,	15°
115	,,	,,	,,	25°
227	,,	,,	,,	46°
263	,,	,,	,,	60°
333	,,	,,	,,	100°

The specific gravities of solutions of ferrous sulphate solutions vary with the strength in accordance with the following table:—

Percentage of crystallized salt.			Specific gravity of solution at 15°.
5	...	...	1·0267
10	...	...	1·0537
15	...	...	1·0823
20	...	...	1·1124

Percentage of crystallized salt.	Specific gravity of solution at 15°.
25	1·1430
30	1·1738
35	1·2063
40	1·2391

The salt is insoluble in absolute alcohol.

Iron sulphate is used in agriculture mainly as a fungicide, occasionally as a disinfectant, as a manure,* and as a veterinary medicine.

In recent years it has been largely employed as a means of destroying charlock and runch, being used as a spray in the same manner as copper sulphate. The strength of the solution to be employed varies slightly with the age of the charlock at the time of spraying.

If the plants be treated when young, a 10% solution is probably best, while for older plants a 15% solution will generally be advisable; in both cases the liquid should be sprayed at the rate of about 40 gallons per acre. Mixtures of the finely-divided dry salt with marl, applied as a powder, have been tried, but with little success.† As is the case with copper sulphate, iron sulphate appears to have a stimulating effect upon cereals, and many results, among others those obtained in the experiments conducted under the supervision of the Yorkshire College and the East and West Ridings Joint Agricultural Council in 1899, seem to show that, even where no charlock or runch may be present, the cereal crop is benefited by spraying.‡

For severe cases of fungoid diseases, in vines, &c., a strong solution of ferrous sulphate to which about 1% of free sulphuric acid has been added is said to be very effective.

Ferrous sulphate, like copper sulphate, is a plant poison, and its success as a fungicide (indeed, probably that of all substances used in that capacity) is probably due to the fact that the fungi are more susceptible to its action, because of their thinner walls, than the higher plants.

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* *v.* p. 170. † Jahresbericht über Agricultur-Chemie 1901, 352

‡ This effect may be either a direct manurial one, an indirect one by promoting the disintegration of the minerals in the soil, or by increasing the chlorophyll production, or, lastly, be due to the destructive action of the salt upon fungoid pests.

Mercuric Chloride, $HgCl_2$, *corrosive sublimate.*—This well-known, poisonous substance is one of the best disinfectants.

Since it is practically non-volatile at ordinary temperatures it can only be applied in solution and must come into actual contact with the infected material. A solution of 1 part in 10,000 is sufficient to kill many micro-organisms, though many spores, *e.g.*, those of anthrax, require a 1% solution. According to Lingard,* a solution of 1 part in 960 destroys the tubercular bacillus in from four to eight hours. Mercuric chloride combines with albuminoid substances to form insoluble compounds, and this fact sometimes interferes with its success as a disinfectant of matter containing proteids. It is said that in such cases the addition of a mineral acid, *e.g.*, hydrochloric acid, or even of tartaric acid, to the solution greatly increases its effectiveness. Recent experiments† throw some doubt on this point. Mercuric chloride is a heavy crystalline substance. Its solubility in water is greatly affected by temperature. 100 parts of water dissolve—

5·73	parts of the	salt at	0°
6·57	,,	,,	10°
7·39	,,	,,	20°
53·96	,,	,,	100°

It is also soluble in alcohol, ether, and glycerine. The salt melts at 288° and volatilises at 303°; its vapour is very poisonous.

Mercuric chloride is largely employed in surgery as an antiseptic, solutions containing from 1 in 1000 to 1 in 10,000 being used.

Mercuric iodide, HgI_2, and cyanide, $Hg(CN)_2$, are also employed as disinfectants.

Mercury salts and mercury vapour are very poisonous to plants, mercury even at the ordinary temperatures giving off into the air sufficient vapour to kill many plants.‡

Plant Poisons.—A great many substances act as plant poisons. Some, however, which when in solution are most deadly in their effects, are converted by substances present in soil into insoluble and almost harmless compounds. Others remain in a soluble form in the water of the soil for some time, and therefore are very effective as destroyers of plants.

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* Quoted by Blyth, A Manual of Public Health, 1890.

† Clark, Jour. Chem. Soc. 1901, abst. ii. 526.

‡ Dafert, Jour. Chem. Soc 1901, abst. ii. 269.

Almost any soluble salt if applied in strong solution will generally kill plants, probably by producing plasmolysis.

Soluble sulphides, sulphocyanides, and sulphites are extremely powerful poisons and can be used as weed-killers. Even strong brine is effective for this purpose.

Coupin investigated the poisonous effect of a large number of salts,* and determined the minimum strength of a solution which had an injurious effect in hindering (not preventing) the growth of the roots of wheat during the first 15 days.

The following are some of his results, the strengths given being the weakest which had an apparent effect:—

Copper sulphate	...	1 in 700,000,000
Mercuric chloride	...	1 in 30,000,000
Cadmium chloride	...	1 in 10,000,000
Silver nitrate ...	...	1 in 1,000,000
Zinc sulphate ...	...	1 in 40,000
Lithium chloride	...	1 in 12,000
Calcium iodide	...	1 in 10,000
Barium nitrate	...	1 in 4,200
Borax ...	...	1 in 1,000
Manganese chloride	...	1 in 1,000
Calcium bromide	...	1 in 400
Calcium chloride	...	1 in 260

In all cases the salts are assumed to be anhydrous. The very minute quantity of copper sulphate which produces a poisonous effect is remarkable—a quantity such as no ordinary chemical test would detect.

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* Compt. Rend. 1901, 645; J.C.S. 1901, abst. ii. 355

APPENDIX.

TABLE OF ATOMIC WEIGHTS OF THE ELEMENTS as given by a Committee of the German Chemical Society,[*] calculated on the assumption that the atomic weight of oxygen is 16·000 :—

Aluminium	Al	27·1	Iron	Fe	55·9
Antimony	Sb	120	Lanthanum	La	138
Argon	A	39·9	Lead	Pb	206·9
Arsenic	As	75	Lithium	Li	7·03
Barium	Ba	137·4	Magnesium	Mg	24·36
Beryllium	Be	9·1	Manganese	Mn	55·0
Bismuth	Bi	208·5	Mercury	Hg	200·3
Boron	B	11	Molybdenum	Mo	96·0
Bromine	Br	79·96	Neodymium	Nd	143·6
Cadmium	Cd	112·4	Nickel	Ni	58·7
Cæsium	Cs	133	Niobium	Nb	94
Calcium	Ca	40·1	Nitrogen	N	14·04
Carbon	C	12·00	Osmium	Os	191
Cerium	Ce	140	Oxygen	O	16·000
Chlorine	Cl	35·45	Palladium	Pd	106
Chromium	Cr	52·1	Phosphorus	P	31·0
Cobalt	Co	59	Platinum	Pt	194·8
Copper	Cu	63·6	Potassium	K	39·15
Erbium	Er	166	Praseodymium	Pr	140·5
Fluorine	F	19	Rhodium	Rh	103·0
Gallium	Ga	70	Rubidium	Rb	85·4
Germanium	Ge	72	Ruthenium	Ru	101·7
Gold	Au	197·2	Samarium	Sa	150
Helium	He	4	Scandium	Sc	44·1
Hydrogen	H	1·008	Selenium	Se	79·1
Indium	In	114	Silicon	Si	28·4
Iodine	I	126·85	Silver	Ag	107·93
Iridium	Ir	193·0	Sodium	Na	23·05

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[*] Berichte der deut. chem. Gesell. 1902.

Strontium	Sr	87·6	Tungsten	W	184
Sulphur	S	32·06	Uranium	U	239·5
Tantalum	Ta	183	Vanadium	V	51·2
Tellurium	Te	127·6	Ytterbium	Yb	173
Thallium	Tl	204·1	Yttrium	Y	89
Thorium	Th	232·5	Zinc	Zn	65·4
Tin	Sn	118:5	Zirconium	Zr	90·7
Titanium	Ti	48·1			

In addition, Krypton, 81·8, Neon, 20, Xenon, 128, Gadolinium, 156, and Thulium, 171, are to be added to the table.

THE CONNECTION BETWEEN VARIOUS HYDROMETER SCALES AND THE TRUE SPECIFIC GRAVITIES OF LIQUIDS.

In England, for technical purposes, Twaddle's hydrometer is often employed. This applies to liquids heavier than water.

The relation between degrees Twaddle and true specific gravity is such that 0° T. corresponds to a specific gravity of 1, while the general formula is—

$$d = \frac{\frac{n}{2}+100}{100}, \text{ or } n = 200\,(d-1)$$

where d = true specific gravity
and n = degrees Twaddle.

Twaddle's hydrometers are, perhaps, based upon a more rational system than most of the other hydrometers. The determinations should be made at 15·5°.

In France, Baumé's hydrometers are in general use. For liquids heavier than water a hydrometer which sinks to 0° in pure water and to 10° in a 10 % solution of common salt, both at 17·5° C., is employed and a uniform scale engraved on the stem.*

For liquids lighter than water, an instrument which sinks to the zero point in a solution of one part of common salt in nine parts of water, and to a point marked 10° in pure water, is constructed and the graduation extended as before.

---

* Most of the modern Baumé's instruments are so constructed that in water they read 0° at 15° C. and in sulphuric acid of sp. gr. 1·8427 they read 66°.

Baumé hydrometers are purely empiric, and have nothing to recommend them; it is desirable that they should be abolished, but inasmuch as they are still extensively used in France and, to some extent, in America, it may be advisable to give the connection between their readings and true specific gravity.

The following formulæ connect together these values:—

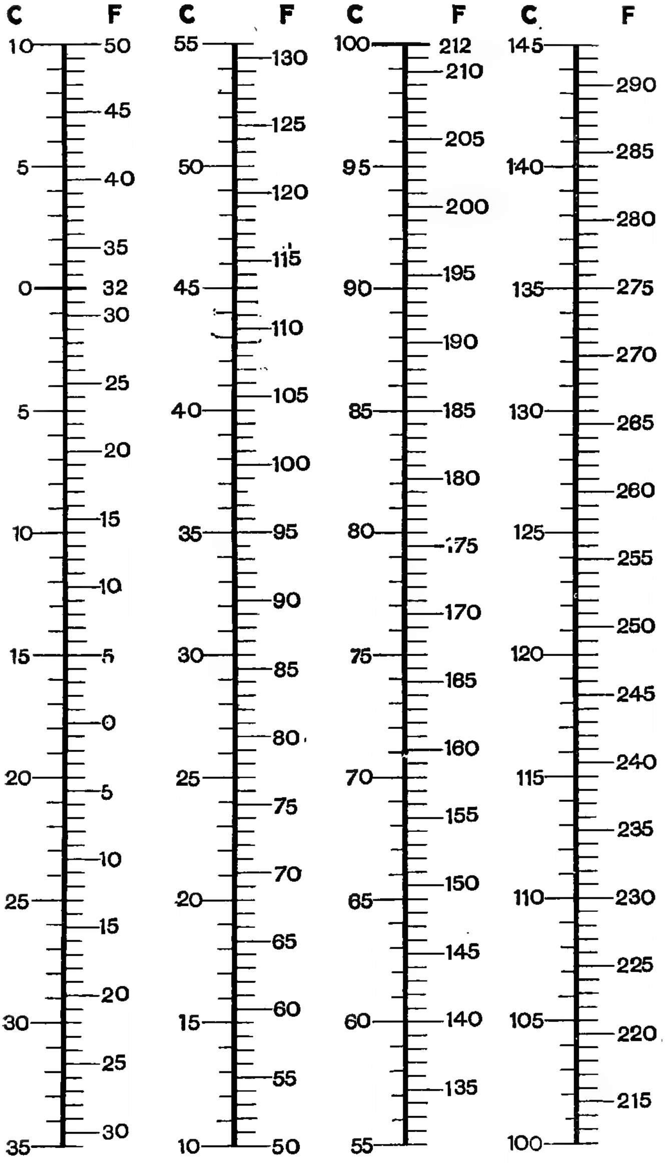
	For liquids heavier than water.	For liquids lighter than water.
At 12·5° C.	$d = \frac{145{\cdot}88}{145{\cdot}88 - n}$	$d = \frac{145{\cdot}88}{135{\cdot}88 + n}$
At 15° C.	$d = \frac{146{\cdot}3}{146{\cdot}3 - n}$	$d = \frac{146{\cdot}3}{136{\cdot}3 + n}$
At 17·5° C.	$d = \frac{146{\cdot}78}{146{\cdot}78 - n}$	$d = \frac{146{\cdot}78}{136{\cdot}78 + n}$

Other hydrometers are employed for special purposes. The principal ones in use are given in the following table:—

Hydrometer.	Liquids heavier than water.	Liquids lighter than water.
Brix (Prussian) at 12·5° R. = 15·62 C.	$d = \frac{400}{400 - n}$	$d = \frac{400}{400 + n}$
Balling	$d = \frac{200}{200 - n}$	$d = \frac{200}{200 + n}$
Gay-Lussac, at 4° ...	$d = \frac{100}{100 - n}$	$d = \frac{100}{100 + n}$
Beck, at 12·5° ...	$d = \frac{170}{170 - n}$	$d = \frac{170}{170 + n}$
Cartier, at 12·5° ...	$d = \frac{136{\cdot}8}{126{\cdot}1 - n}$	$d = \frac{136{\cdot}8}{126{\cdot}1 + n}$

Conversion of Temperatures from one Thermometric Scale to another.

In this book all temperatures are stated in the Centigrade scale, and it is to be regretted that the Fahrenheit thermometer is still commonly employed in England. Though the relationship between the two is comparatively simple, it is troublesome and confusing to have two scales in use. It is perhaps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hardly necessary to state here that the interval of temperature between the melting point of ice and the maximum condensing temperature of saturated aqueous vapour at the normal pressure, is divided in the Centigrade scale into 100 equal parts or degrees, in the Fahrenheit scale into 180 degrees, and that the scale commences from the melting point of ice in the former, but from a point 32° below this temperature in the latter. Hence the equations—

$$°\text{C.} = \tfrac{5}{9}\,(°\text{F.} - 32)$$
$$\text{and } °\text{F.} = \tfrac{9}{5}\,°\text{C.} + 32.$$

Though these formulæ are simple enough and easily remembered, when many conversions have to be made they are troublesome. A graphical method of connecting the two has been found very convenient in practice, and the diagram on p. 385 will be useful, as it enables a temperature expressed in either scale to be converted into the corresponding temperature in the other scale, without the trouble of interpolation. The graduations extend from −35° C. (−31° F.) to 145° C. (293° F.) commencing in the lower left-hand corner and increasing in all cases as the stem is ascended.

TABLE OF THE SOLUBILITIES OF VARIOUS SALTS IN WATER.

The following table, giving the solubility of certain salts used in agriculture, may be useful. One hundred parts by weight of water at the temperatures stated dissolve the following parts by weight of the various salts*:—

	At 10°.	At 100°.
Alum, ammonia, $(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$	9·2	422·0
,, potash, $K_2SO_4.Al_2(SO_4)_3.24H_2O$ ...	9·5	357·5
Ammonium chloride, NH_4Cl	33·3	77·3
,, sulphate, $(NH_4)_2.SO_4$ ...	73·0	103·3
Borax, $Na_2B_4O_7.10H_2O$	4·6	201·4
Boric acid, H_3BO_3	2·9	34·0
Calcium carbonate, $CaCO_3$ ... about	0·0013	?
,, ,, (in water saturated with CO_2 at 21°) ...	0·099	
,, hydrate, CaH_2O_2	0·177	0·0766

---

* Taken chiefly from Comey—A Dictionary of Solubilities, 1890.

	At 10°.	At 100°.
Calcium sulphate,* $CaSO_4.2H_2O$	0·246	0·182
Copper sulphate, $CuSO_4.5H_2O$	36·0	203·2
Ferrous sulphate, $FeSO_4.7H_2O$	34·5	122·0
Magnesium sulphate, $MgSO_4.7H_2O$	96·0	670·0
Potassium carbonate, K_2CO_3	109·0	156·0
,, chloride, KCl	32·0	56·0
,, nitrate, KNO_3	21·1	247·0
,, sulphate, K_2SO_4	9·7	26·2
,, chloroplatinate, K_2PtCl_6	0·9	5·2
Sodium bicarbonate, $NaHCO_3$	8·15	decomposes
,, carbonate, Na_2CO_3†	12·06	45·4
,, ,, $Na_2CO_3.10H_2O$	40·9	538·0
,, chloride, NaCl	35·8	39·8
,, nitrate, $NaNO_3$	80·1	180·0
,, phosphate, $Na_2HPO_4.12H_2O$	about 9	melts below 100°
,, sulphate, $Na_2SO_4.10H_2O$‡	about 23	241·0
,, sulphate, Na_2SO_4.	9·0	42·5

THE BRITISH AND METRIC SYSTEMS OF UNITS OF LENGTH, AREA, VOLUME, AND WEIGHT.

The inconvenience and cumbrousness of our British system of weights and measures have too often been pointed out to need further reference here; but in agricultural matters, perhaps, more than in other commercial branches, the inconsistencies of the current systems of units are strikingly evident. In addition to the disadvantages common to all our measures and weights, there are such anomalies as selling grain nominally by volume (bushels and quarters) and then fixing definite weights for these volumes, necessarily different for different kinds of grain, and what is even worse, different in different districts. However, custom in these matters is so powerful that it will probably be long before such anomalies are abolished.

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* Most soluble in water at 35°; 0·279 parts then dissolve.

† Is most soluble about 38°, when 100 parts of water dissolve 51·67 parts of the anhydrous salt or 1142 parts of the soda crystals.

‡ Is most soluble about 33°, when about 412 parts of the decahydrated or 50·6 of the anhydrous salt dissolve.

The fundamental units and method of decimal multiples and sub-multiples of the Metric system are doubtless sufficiently familiar already to the reader. The connection between the metric units of length, area, volume, and weight and those of the British system will therefore only be given here:—

Units of length.

The metre = 39·3708 inches = 3·2809 feet = 1·0936 yards.

The kilometre = 3280·9 feet = 1093·63 yards = 0·62138 mile.

Or 1 inch = 2·53995 centimetres
1 foot = 0·30479 metre
1 yard = 0·91438 metre
1 mile = 1·609315 kilometres.

Units of area.

1 sq. metre = 1550 sq. inches = 10·764 sq. feet = 1·196 sq. yards.

1 are = 100 sq. metres = 1076·4 sq. feet = 119·6 sq. yards = 0·0247 acre.

1 hectare = 11960 sq. yards = 2·4711 acres.

Or 1 sq. inch = 6·45137 sq. centimetres
1 sq. foot = 9·290 sq. decimetres = 0·0929 sq. metre
1 sq. yard = 0·8361 sq. metre
1 acre = 0·40467 hectare = 4046·7 sq. metres.

Units of capacity.

1 cubic centimetre = 0·061 cb. inch.

1 cubic decimetre or 1 litre = 61·028 cb. inches = 1·76 pints = 0·22 gallon.

1 cubic metre, 1 kilolitre, or 1 stere = 61028 cb. inches = 35·317 cb. feet = 1·308 cb. yards = 220·09 gallons = 27·512 bushels.

Or 1 cb. inch = 16·3862 cb. centimetres
1 cb. foot = 28·3153 litres
1 pint = 567·93 cb. centimetres
1 gallon = 4·54346 litres
1 cb. yard = 0·7645 stere or 764·513 litres
1 bushel = 36·3477 litres.

Units of weight.

1 gramme = 15·43235 grains = 0·035274 ounce Avoirdupois.

1 kilogram = 35·2739 ounces Avoirdupois = 32·1507 ounces Troy = 2·2046 pounds Avoirdupois.

1 metric tonne = 1000 kilos = 2204·621 pounds Avoirdupois.
= 0·98420 ton.

Or 1 ounce Avoirdupois = 28·3495 grammes
1 ounce Troy = 31·1035 ,,
1 pound Avoirdupois = 453·593 ,,
1 hundredweight = 50·802 kilograms
1 ton = 1016·05 ,,

On the Continent, crop yields or manurial dressings are frequently expressed in kilograms per hectare; in England, in pounds or tons per acre. The following connection between the two systems may therefore be found useful:—

To convert kilograms per hectare into pounds per acre multiply by 0·89222.

To convert pounds per acre into kilograms per hectare multiply by 1·1208.

To convert kilograms per hectare into tons per acre multiply by 0·0003984.

To convert tons per acre into kilograms per hectare multiply by 2510·9.

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